Catalytic Chemical Vapor Deposition of Carbon Nanotubes for Field Emission and Field Effect Transistor Applications

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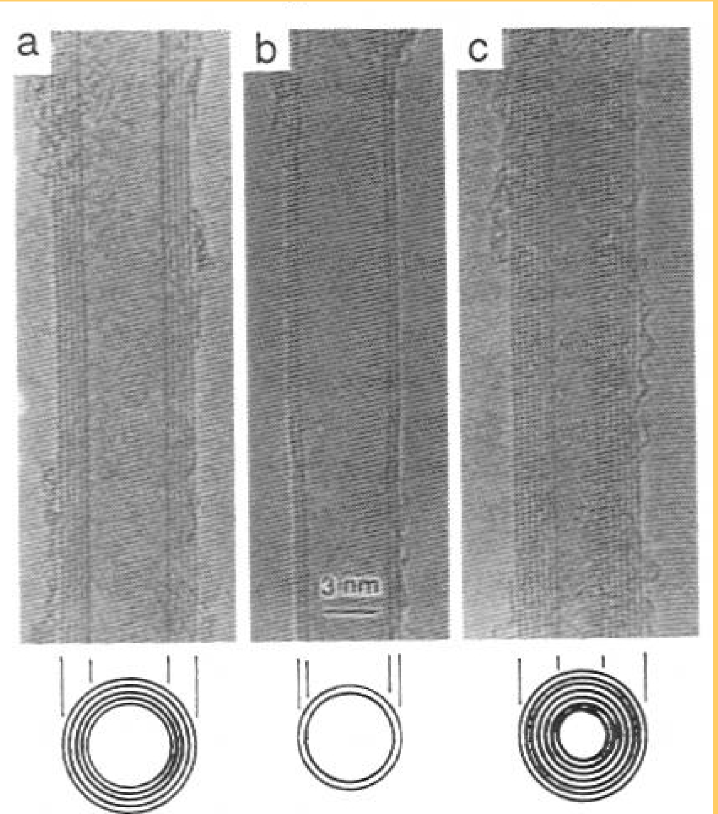
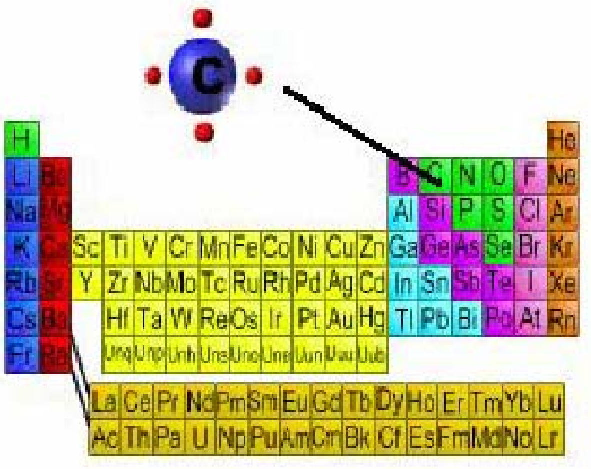
May 10, 2006 Dept. of Physics, NTHU

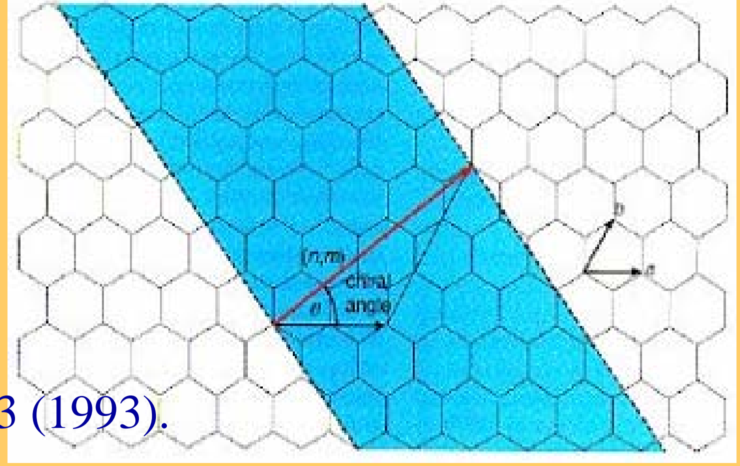
First Discovery of Carbon Nanotubes by Prof. Sumio Iijima

Multi-wall carbon nanotubes (MWNTs) were first directly imaged by HRTEM by S. Iijima, NEC 1991





Sumio Iijima

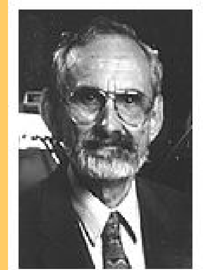


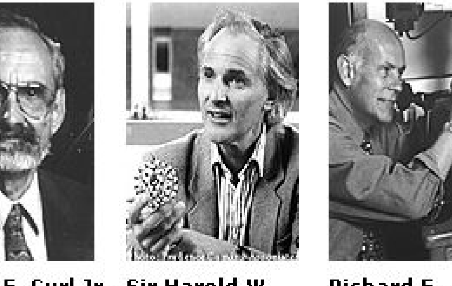
S. Iijima, ***Nature*** **354**, 56 (1991).

S. Iijima and T. Ichihashi, ***Nature*** **363**, 603 (1993).

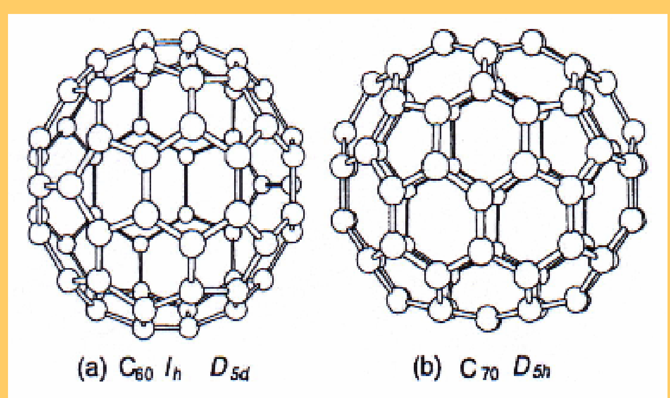
First Discovery of C_{60} Fullerene

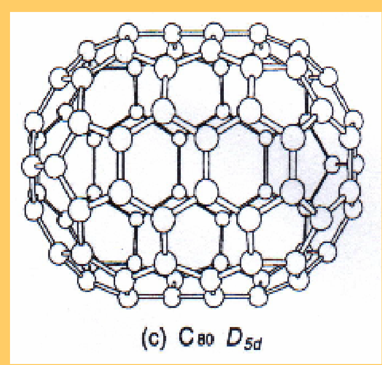
C_{60} "fullerene" was first detected by Laser Vaporization Mass Spectrometry in Harry Kroto, Robert Curl Jr. and Richard Smalley's experiment, Rice University 1985.

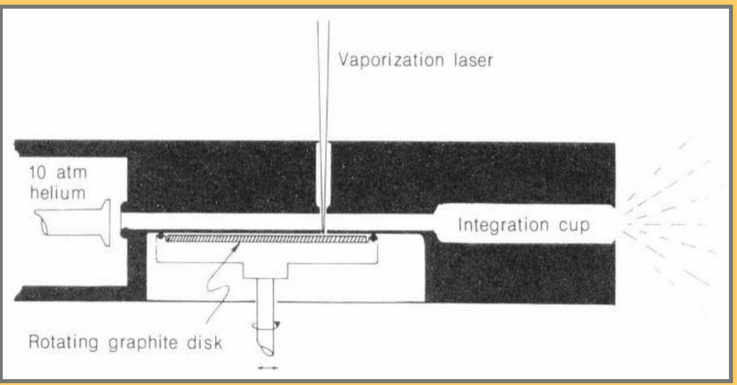


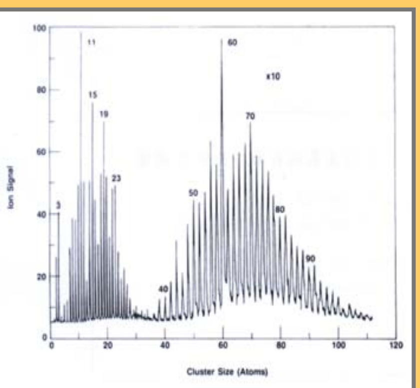


Nobel Prize in Chemistry 1996



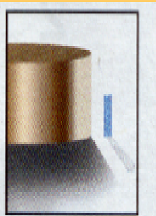






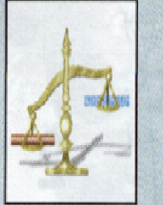
R. Smalley, "Discovering the Fullerenes", Nobel Lecture, Dec. 7, 1996.

Carbon Nanotube Properties and Applications



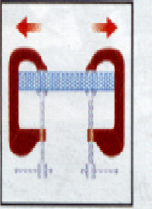
Small sizes

0.4~1.8 nm
(E beam Lithography : 50 nm Wide, 2~3 nm Thick)



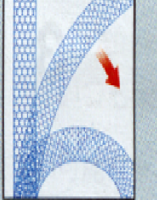
Low Densities

1.33~1.40 g/cm^3
(Al:2.7 g/cm^3)



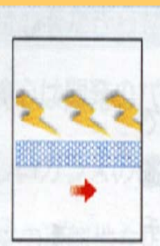
Tensile Strength

45 GPa
(Steel : Broken at 2 Gpa.)



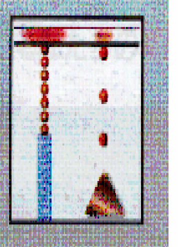
Elastisity

Bending and Recovery
(Metals and carbon fibers are brittle.)



Electric Currents

Approximaely 1 GA/cm^2
(Cu wires : 1 MA/cm^2)

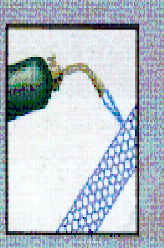


Field Emission of Electrons

1~3 V/μm
(Mo tips : 50~100 V/μm. Short life-times)

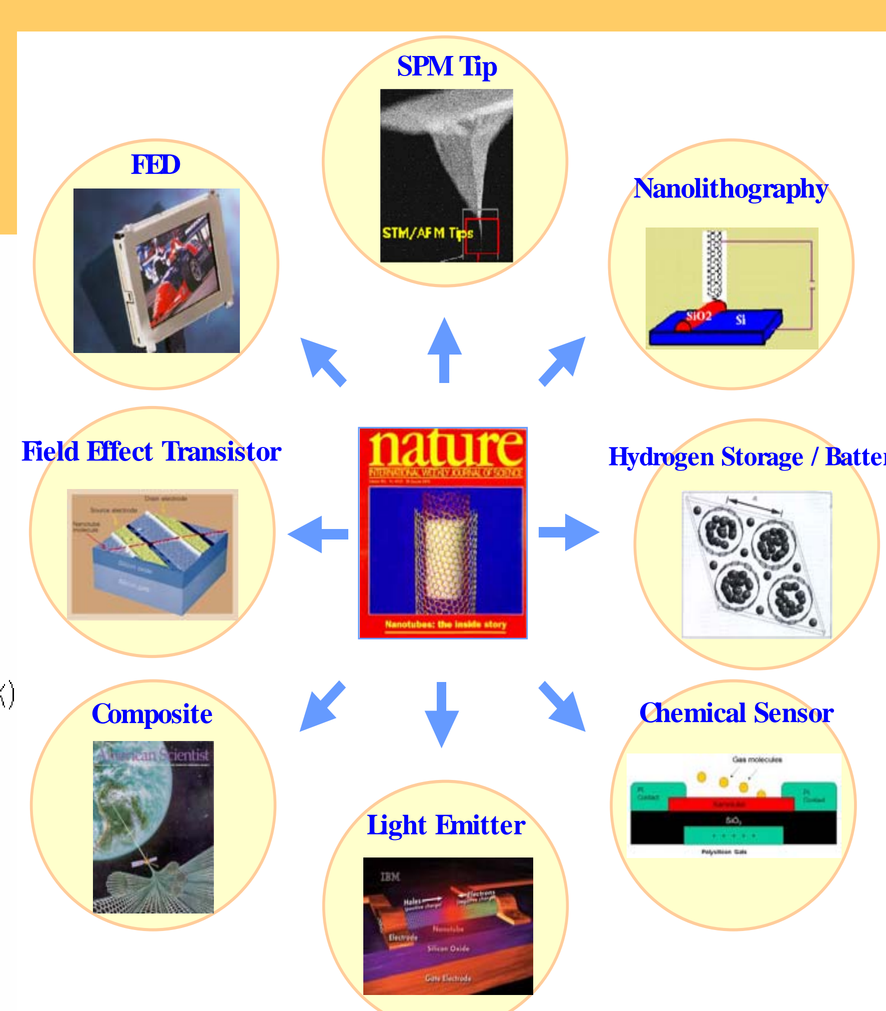
Thermal Conductivities

6000 W/m・K at Room temperature
(Pure diamonds : 3320 W/m・K)



Thermal Resistivities

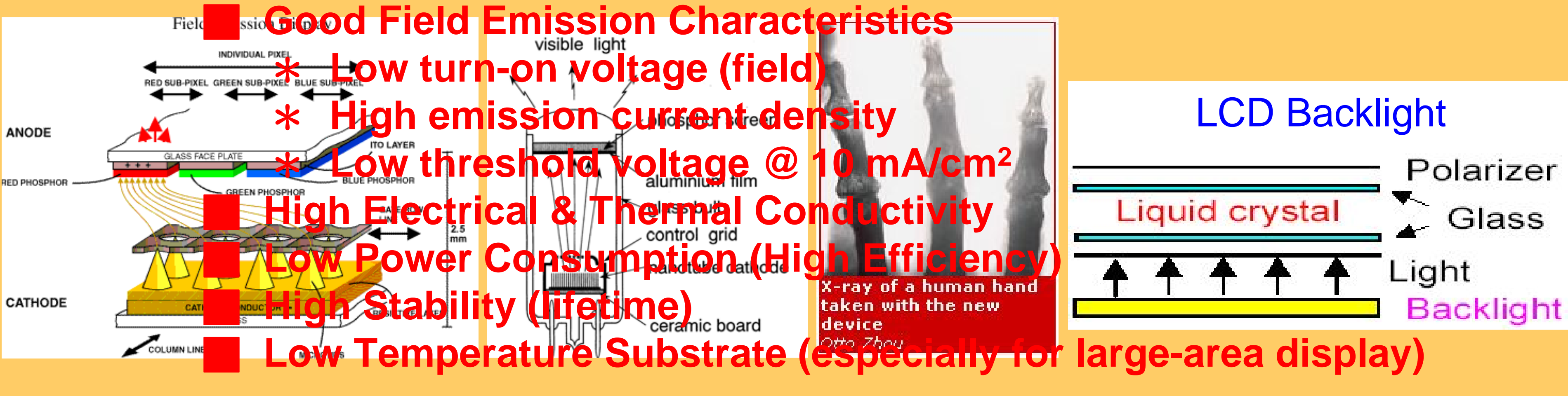
2000℃ in vacuum. 750℃ in Air.
(Cu wires in electronic circuits : 600~1000℃ melting)



Carbon Nanotube-based Nano-electronics

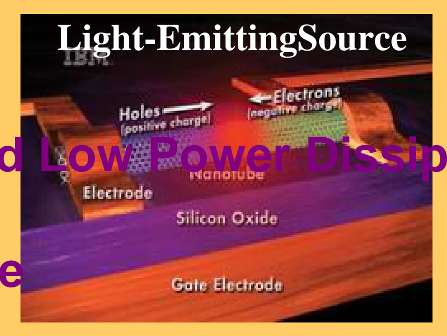
I. Field Emission Electron Source & Devices

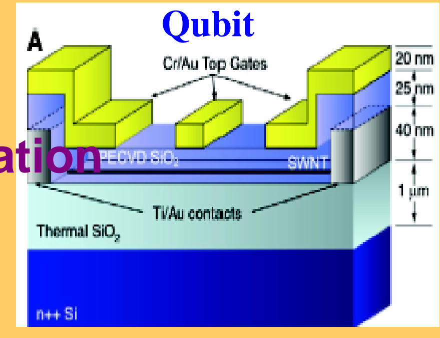
- Good Field Emission Characteristics
  - * Low turn-on voltage (field)
  - * High emission current density
  - * Low threshold voltage @ 10 mA/cm^2
- High Electrical & Thermal Conductivity
- Low Power Consumption (High Efficiency)
- High Stability (lifetime)
- Low Temperature Substrate (especially for large-area display)



II. Field Effect Transistor & Devices

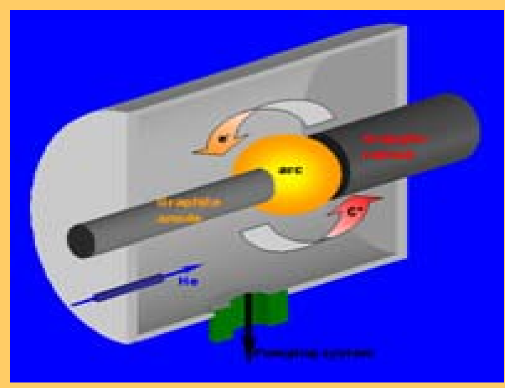
- High Transconductance
- High On-Off Ratio
- High Sub-threshold Swing
- High Thermal Conductivity and Low Power Dissipation
- Good Mechanical Structure
- Good High Speed Performance



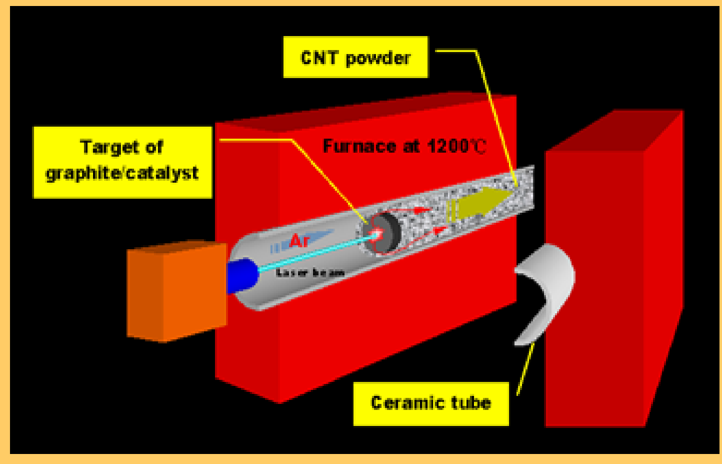


Fabrication Methods for Carbon Nanotubes

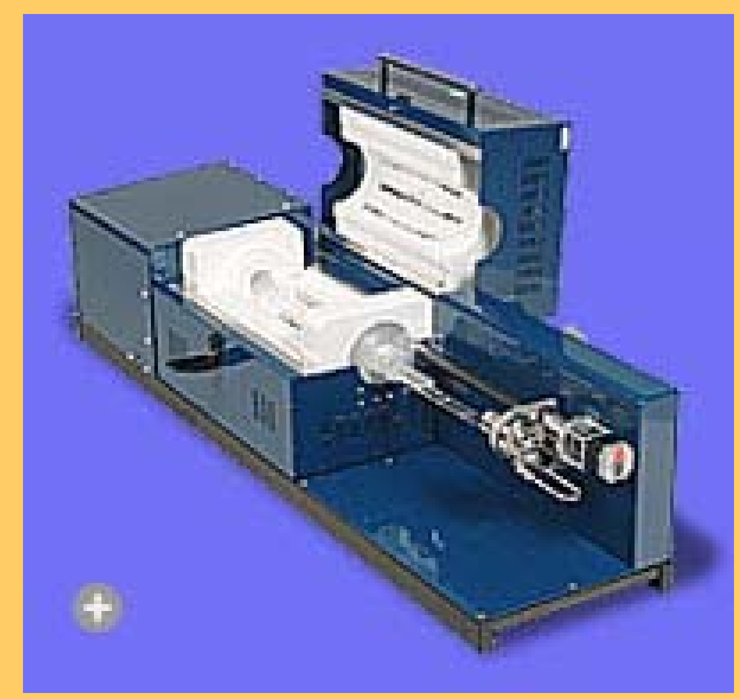
- Arc Discharge



- Laser Ablation



- Chemical Vapor Deposition



Fabrication of CNT Field Emitters

- **Screen Printing**

  Pre-fabricated CNTs
  → transferred onto substrates
  (unordered films)

- ***in-situ* Catalytic CVD Growth**

  as-grown CNTs on substrates
  → vertically-aligned or unordered

Anode

Cathode

Phosphor → ITO glass → Prototype CNT-FED

Ag Nanopowder → CNT Paste

Binder → CNT Paste

Carbon Nanotubes → Purification → CNT Paste

CNT Paste → Patterning → Vacuum Baking → Prototype CNT-FED

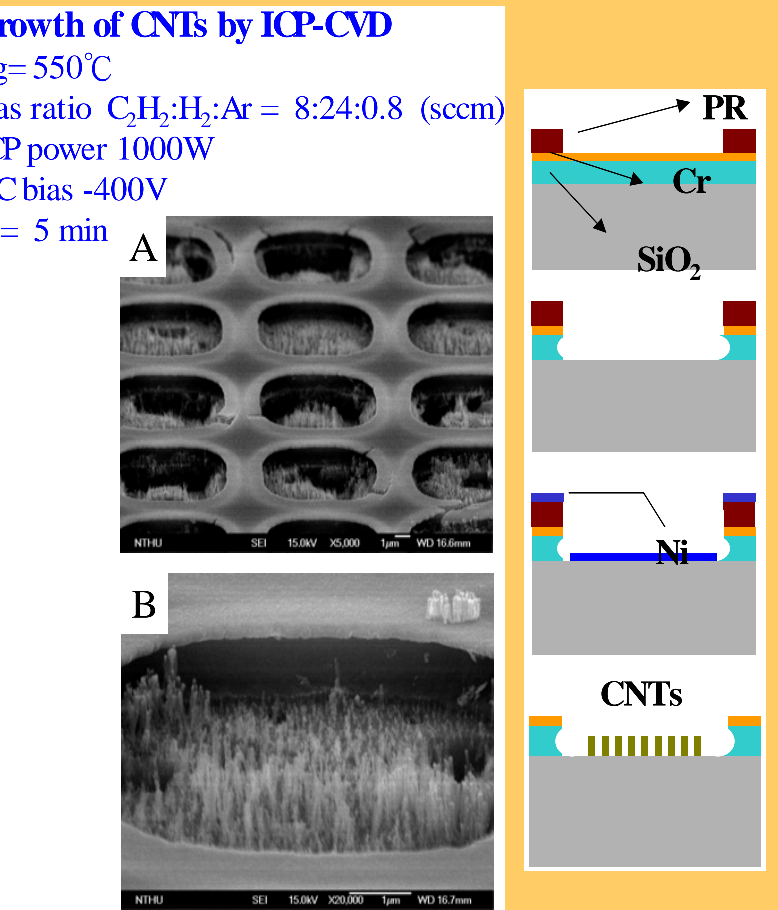
CNT

ERSO

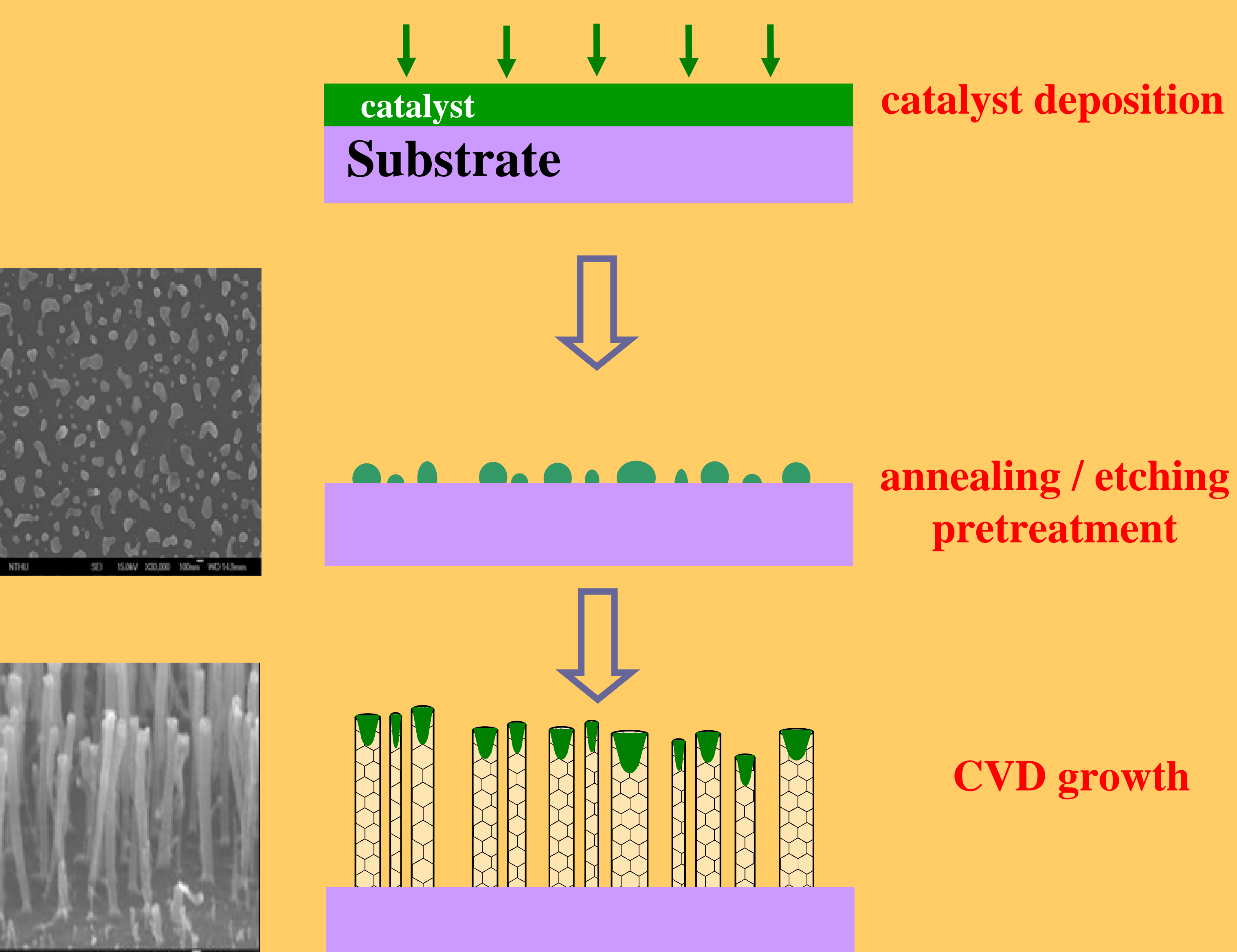
2001/9

(H.J. Lai, 2002 Hsinchu Materials Nanotechnology Forum)

4" fully-sealed multi-color CNT-FED, Resolution=21(RGB)x256, Vac<220V, Brightness=150nits, Eff.=2 lm/W



Growth of Carbon Nanotube by Catalytic CVD



Synthesis of Carbon Nanotubes by Thermal CVD

Furnace Temperature: < 1100 ℃
Pressure: 5 torr~1atm
Gas: Ar, NH_3, CH_4, C_2H_2

10 nm Ni / Si(100)
800°C, 1 atm, NH_3 pretreated,
$C_2H_4/NH_3/Ar$ (10/20/70 sccm)
10 mins growth

Z.Y. Juang et al, *Diamond and Related Materials* 13 (2004) 1203.
W.Y. Lee et al, *Diamond and Related Materials* 13 (2004) 1232.
Z.Y. Juang et al, *Diamond and Related Materials* 13 (2004) 2140.

Synthesis of Carbon Nanotubes by Plasma-enhanced CVD

Gas Panel

Power supplies

Vacuum system controllers

High density plasma
RF 13.56 MHz 2500W
Pressure 10 ~ 100 mTorr
Gas: Ar, H_2, C_2H_2, NH_3, N_2
DC/RF bias
Sub. Temp. (PBN/PG): < 1000 ℃

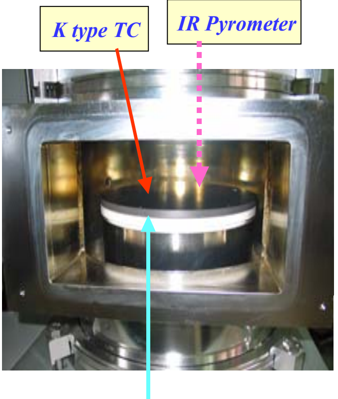
ICP Chamber

Process Chamber

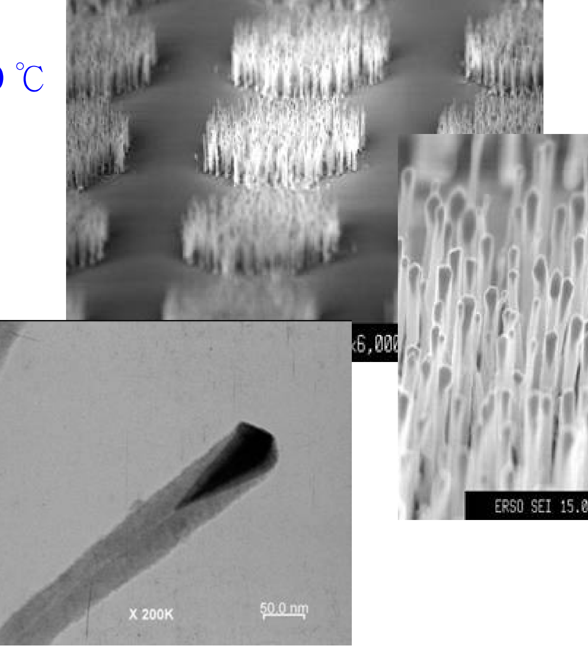
Automatic Process Control
In situ Diagnostic:

- Langmuir Probe
- Optical Emission Spec.
- Quadruple Mass Spec.
- Impedance Meter

K type TC *IR Pyrometer*



R type TC



10 nm Ni /Si (100)
ICP 1000 W, 17mTorr, 550 ℃
C_2H_2 : H_2 = 8 : 24 sccm, bias –400 V
10 min growth

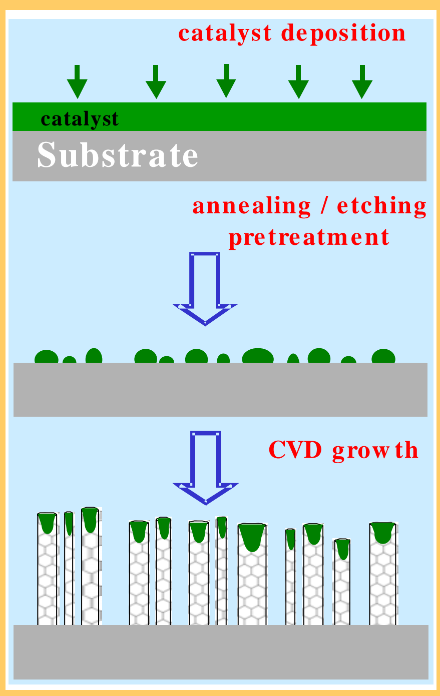
C.H. Weng et al, *Appl. Phys. Lett.* 85 (2004) 4732.
H.W. Wei et al. *J. Appl. Phys.* (2005) in press.
C.H. Tsai et al, *Thin Solid Film* (2005) in press.

Parametric Study of Catalytic CVD

Thermal CVD

Effects of:

- Type of Catalyst
- Catalyst film thickness
- Carbon source gas (CH_4, C_2H_4, C_2H_2)
- Feed gas flow rate / ratio
- Process temperature
- Pressure



ICP - CVD

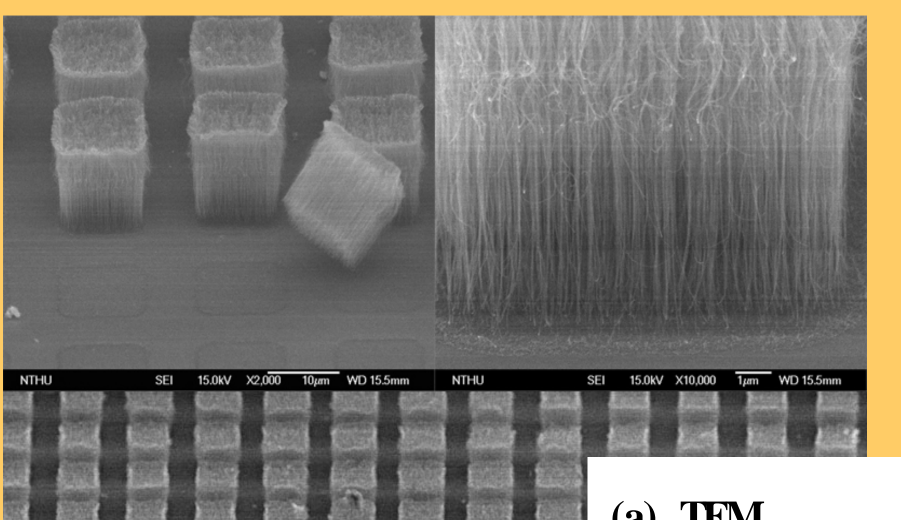
Effects of:

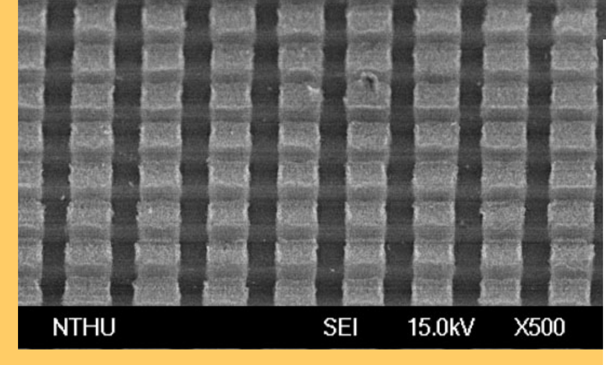
- Bias voltage / power
- ICP power
- Pressure
- Substrate temperature
- Feed gas flow rate / ratio

Objectives:

- Better understanding of growth mechanisms and growth kinetics
- Lower the growth temperature to below stress point of glass (~ 570℃)
- Vertically-aligned and good structure for better field emission
- Good adhesion to substrate and good conductance

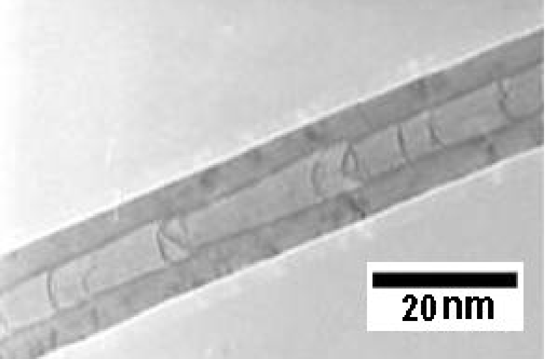
CNT Growth by Thermal CVD



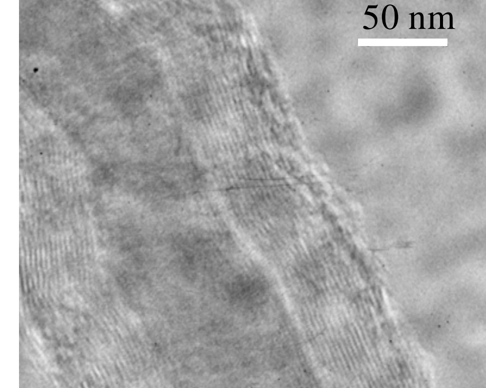


A large area of unifrom patterned well-vertically-aligned CNTs were grown on 10 nm Ni/Si with the optimal growth condition:
$C_2H_4/NH_3/Ar$ = 10/20/70 sccm
800°C, 1 atm, growth time 10 mins

(a) TEM



(b) HR-TEM



- Inner Diameter: ~7 nm
- Outer Diameter: ~20 nm
- wall thickness: ~18 layers
- Inter-layer spacing: 0.34 nm (graphite)

- Base-growth Mode
- Bamboo-like Structure

Kinetics Study of MWNT Growth

Catalyst:
5 nm

Pretreatment:
NH_3/Ar 900℃
5 mins

Growth:
C_2H_4/NH_3
(2:3)/Ar

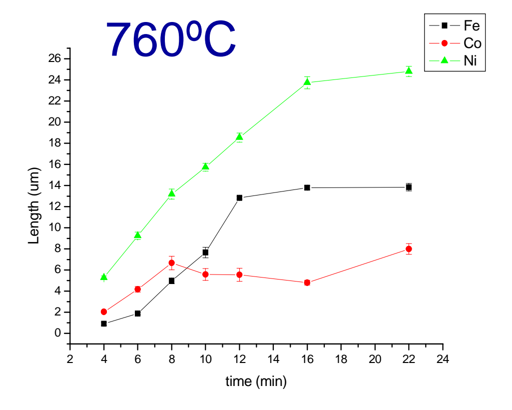
	760˚C (10min)	800˚C (10min)	840˚C (10min)	880˚C (4min)
Fe				
Co				
Ni				

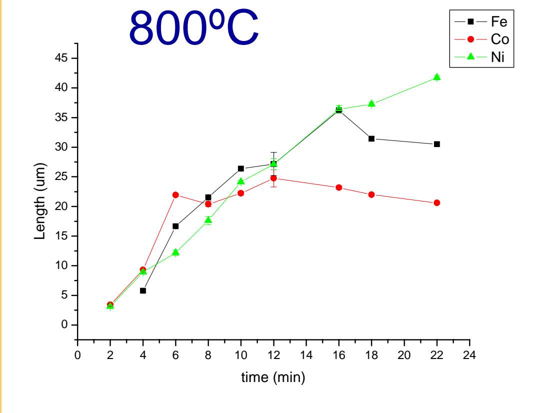
840ºC

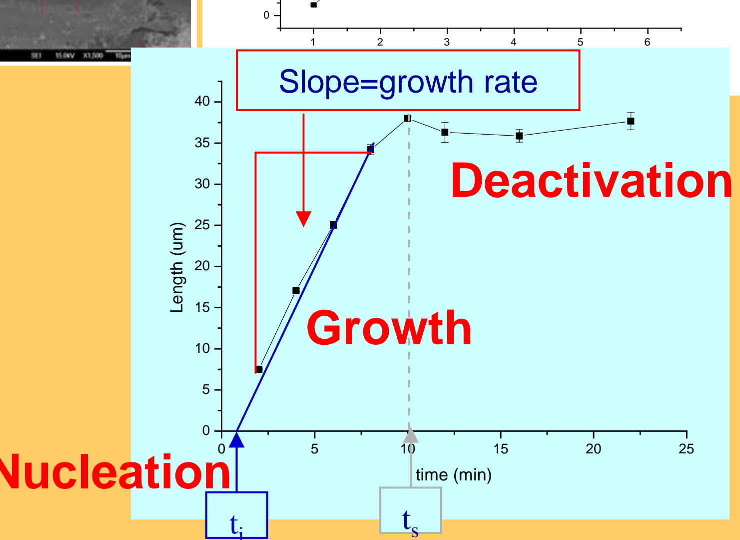
Length (um) vs. time (min) — Fe, Co, Ni

880ºC

Length (um) vs. time (min) — Fe, Co, Ni







Nucleation Stage – Arrhenius plot

	Fe	Co-u	Co-d	Ni-l	Ni-r
range (˚C)	760-840	760-880	760-880	760-880	760-880
slope	19400.8182	18189.31307	11958.88693	6109.76886	13376.11197
q (kcal/mol)	38.4023	36.004	23.672	12.0938	26.4769
Mean q (Kcal/mol)	38.4023	29.838		19.285	
Mean q (ev)	1.6718	1.299		0.8395	

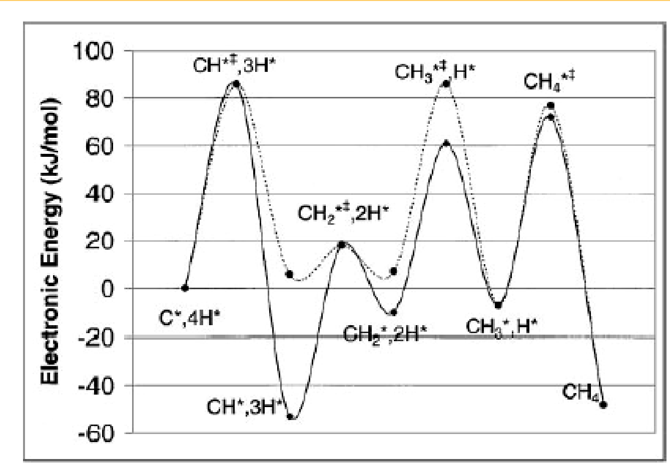


FIG. 6. Electronic energy plot for CH_x species on Ni(111), quantum chemical values (◆) and fitted values (●).

R. M. Watwe et al, Journal of Catalyst 189 (2000) 16-30

Activation energy≒20kcal/mol

C
C
C
C
C
M M M

CNT nuclei

Catalyst surface

Y.A. Mo et al. *6th Int. Conf. on Sci. and Appl. of Nanotubes*, Jun 26-Jul 1, 2005.

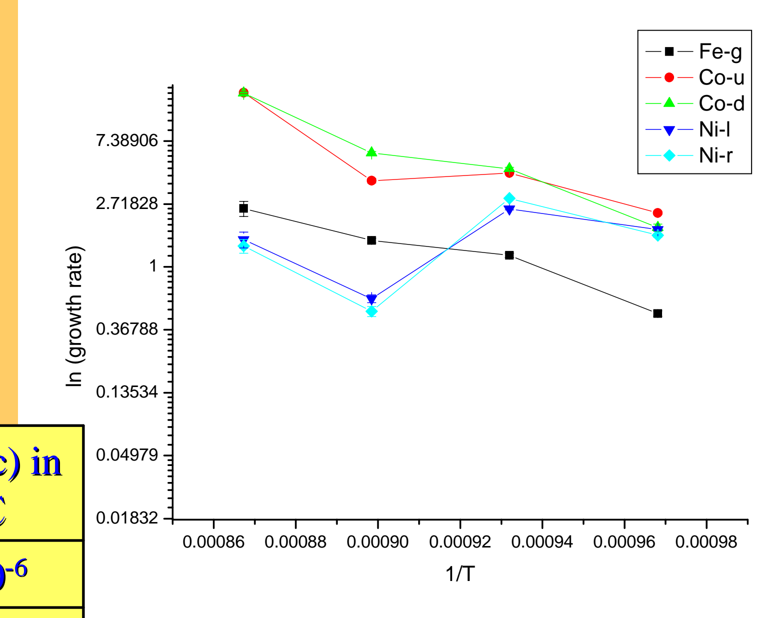
- **Nucleation stage:**

  Process path: nuclei formed by carbon clustering from dehydrogenation of CH_x on catalyst surface.

  Rate control limit: carbon species dehydrogenation rate on catalyst

Growth Stage – Arrhenius plot

Activation energy				
	Fe-g	Co-u	Ni-l	
Temp. range (℃)	760~880	760~880	760~800	840~880
Q(ev)	1.66108	1.57127	1.0991	2.7441



	Q (eV)	$D(cm^2/sec)$ in 900℃	$D(cm^2/sec)$ in 1200℃
Ni, Bulk	1.27ev	$1.12*10^{-7}$	$1.44*10^{-6}$
polycrystalline Ni, Surface	0.3ev	$1.65*10^{-6}$	$3.07*10^{-6}$
Ni(111), Surface	0.5~0.4ev	$1.79*10^{-7}$	$6.19*10^{-7}$
Ni(100), Surface	2.1ev		
Ni(110), Surface	0.4ev		
Fe, Bulk	1.3~1.58ev	$1*10^{-7}$	$1\sim2*10^{-6}$
Fe, Surface	0.1 ev	$1.1*10^{-3}$	$1.5*10^{-3}$
Co, Bulk	1.54ev		

- **Steady Growth:**

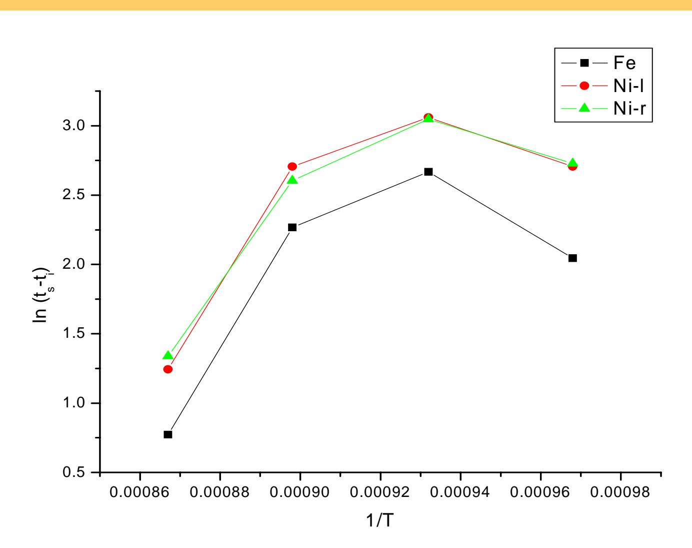
  Process path: Carbon diffuses through catalyst particle by bulk diffusion, until bond with dangling bond of MWNT graphite layer.

  Rate control limit:

  carbon bulk diffusion

Deactivation Stage – Arrhenius plot

catalyst	Fe		Ni	
range	760-800	840-880	760-800	840-880
q(KJ/mol)	-143.76856	400.463322	-77.9052	350.62566
q (Kcal/mol)	-34.23061	95.34841	-18.54886	83.4823
q(ev)	-1.49	4.1508	-0.80748	3.63419



1. In 880~840˚C,the slope is positive, so the carbon which cover the catalyst particle is formed by cracking in gas.

2. In 800~760˚C, the slope is negative, so the carbon which cover the catalyst particle is formed by dehydrogenation on catalyst surface.

3. In 880~840˚C,the slope is much bigger than the slope in 800~760˚C, maybe because the activation energy of formation carbon in gas is large.

4. The ratio of q on Fe to Ni is 1.85 which almost is equal to the ratio of H_2 chemisorption heat on Fe to Ni.

- **Deactivation stage:**

  Process path:

  1. In 880~840°C, active sites covered by carbon formed by cracking in gas adsorbing on catalyst surface.

  2. In 800~760°C, active sites covered by the carbon formed by dehydrogenation on catalyst surface.

  Rate control limit: 1. In 880~840°C, the carbon source species cracking rate.

  2. In 800~760°C, the carbon source species dehydrogenation rate on catalyst.

Thermal CVD Growth on Glass Substrate

- Synthesis temperature lower than stress point of ~570°C is required.

- A conducting metal layer on glass is required.
- Cr was chosen for low resistivity and Ni can form nanoparticle on Cr.

Process Modification:

(1) Two temperature zone approach: not successful.

(2) Single temperature:

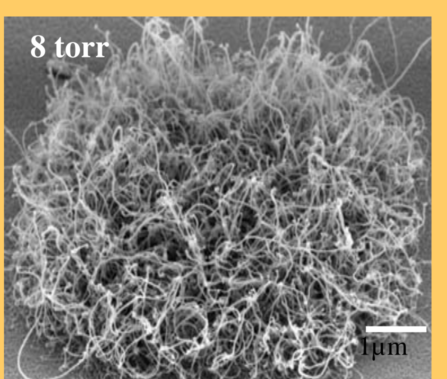
-- lower temperature: low catalysis efficiency → C_2H_2 was chosen; low diffusion rate → low C_2H_2 flow rate and high NH_3/C_2H_2 ratio

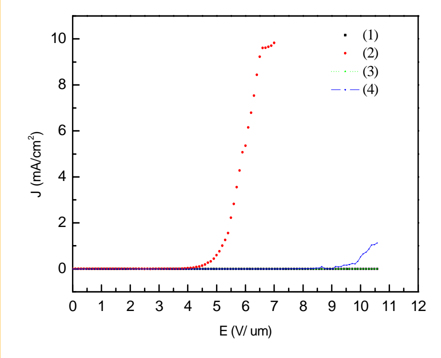
-- A new pumping system was installed to lower the pressure.

TECO Nano.
Condition:
pressure ~2×10^{-5} torr
gap ~70 μm
voltage ~1.1 kV (DC)
peak current ~0.08 mA

Optimal process condition on 10 nm Ni/100 nm Cr/glass:
$C_2H_2/NH_3/Ar$ = 10/50/430 sccm
550°C, 8 torr, growth time 10 mins

J.H. Lee et al, *Surface and Coating Tech* (2005) in press.

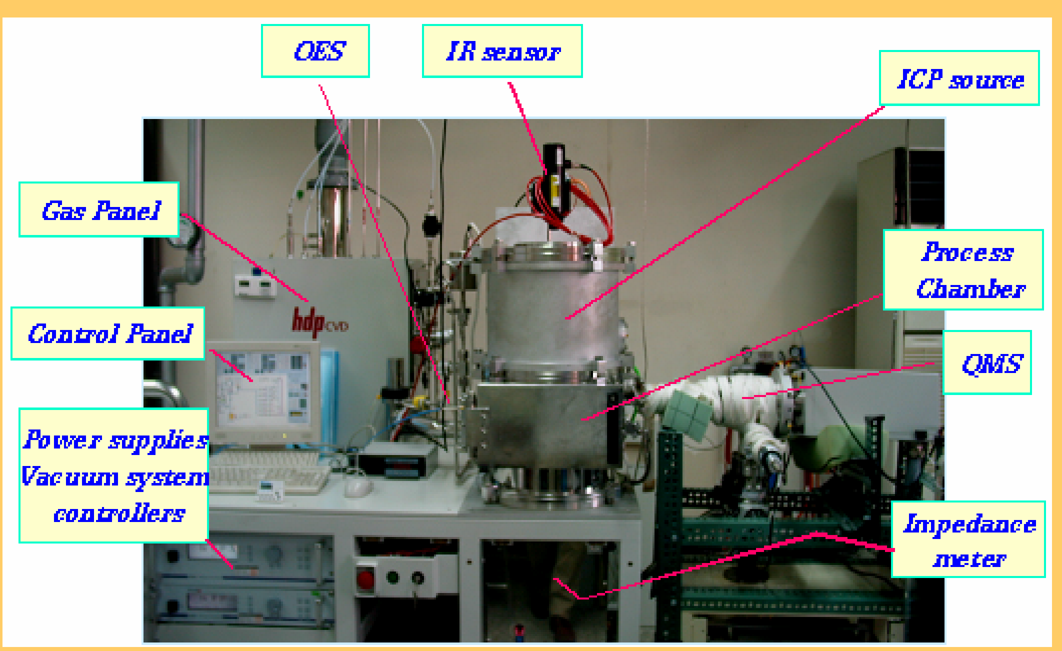




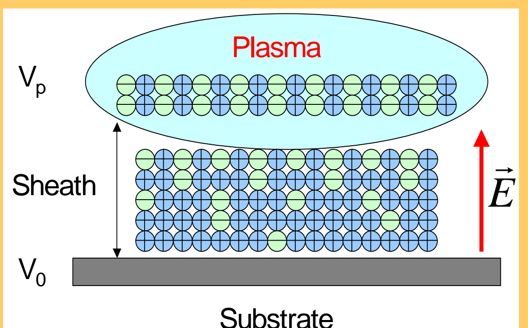
Field Emission:
Turn-on: 3~4 V/μm
Threshold @10 mA/cm^{-2}: ~ 7 V/μm

Controlled Growth of Vertically-aligned Multi-walled Carbon Nanotubes and *in-situ* Pre- / Post- Treatments for Field Emission Enhancement

◆ Inductively-Coupled Plasma CVD



High Density Plasma
RF 13.56 MHz 2500W max.
Pressure 10～100 mTorr
Gas: Ar, H_2, C_2H_2, NH_3, N_2
DC/RF bias: max. 600 V / 600 W
Sub. Temp. (PBN/PG): < 1000 ℃
Sub. size 150 mm

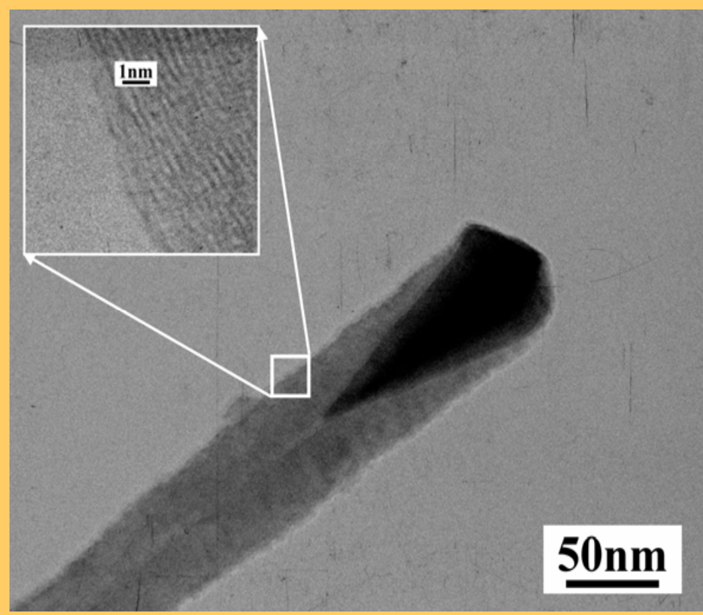


Equipment Novelty:

- **Developed through Industrial-Cooperative Project with a domestic company, Nano Architect Research Co., in Science Park**
- **High Plasma Density (～10^{12} cm^{-3}), Low Pressure (～mTorr), Low Temperature (400～550 ℃)**
- **Independent control of Ion Density and Energy (through ICP power and Substrate DC / RF bias)**
- **Automatic Process Control through *in-situ* Diagnostic (Langmuir Probe, Optical Emission, Quadruple MS, Impedance Meter)**
- **2 Patents on Equipment Design, 2 Patents on Process Control and 12 journal/conference papers**

CNT Growth by ICP- CVD

10 nm Ni/Si
ICP power 1000 W, Pressure 17 mTorr
C_2H_2/H_2 = 8/24 sccm
550°C, growth time 10 mins



- Inner Diameter: ~10 nm
- Outer Diameter: ~80 nm
- wall thickness: ~100 layers
- Inter-layer spacing: ~0.4 nm

- Tip-growth Mode
- Cone-shaped catalyst at tip
- Hollow Tube Structure

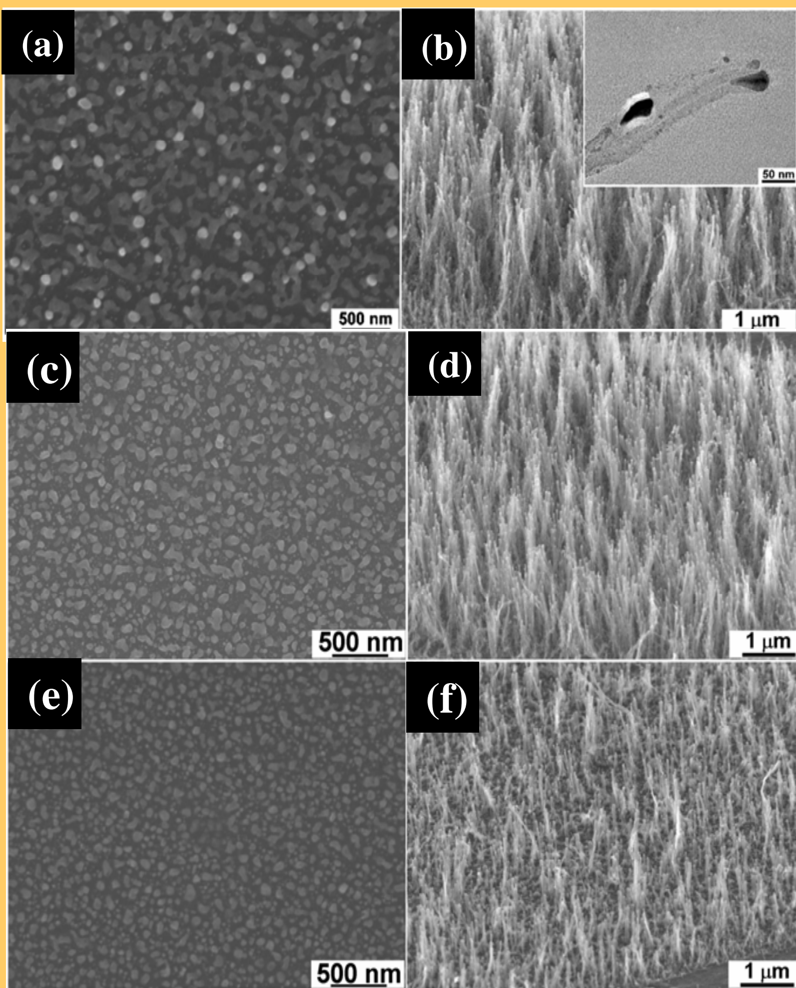
ICP-CVD Growth on Glass Substrate

- Optimal substrate temperature is already lower than glass stress point.
- Cr was also chosen for conducting metal layer.
- Different Ni thickness was tested (Ni = 20, 30, 40 nm).

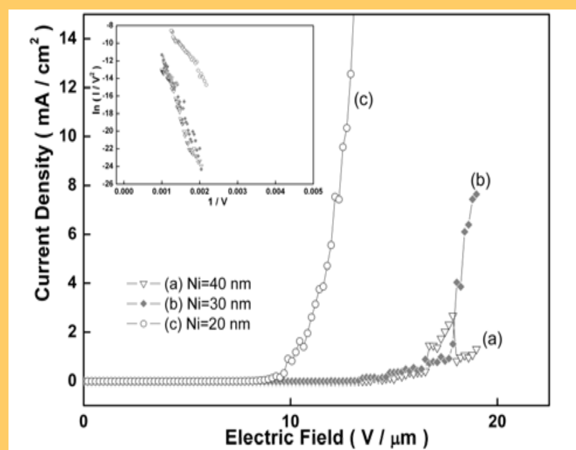
40nmNi/ 60nmCr/ glass

30nmNi/ 60nmCr/ glass

20nmNi/ 60nmCr/ glass



Optimal process condition on 20 nm Ni/ 100 nm Cr/glass:
NH3 plasma pretreated for 5 mins, ICP 500 W, RF bias 300 W, pressure 20 mTorr, $C_2H_2/H_2/Ar = 3/17/0.8$ sccm, 500°C, growth time 20 mins



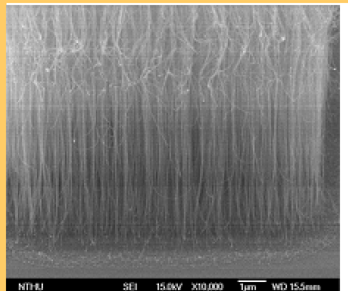
Turn-on: 9~10 V/μm
Threshold @10 mA/cm^{-2} ~12 V/μm

C.H.Tung et al. *Thin Solid Film* (2005) in press.

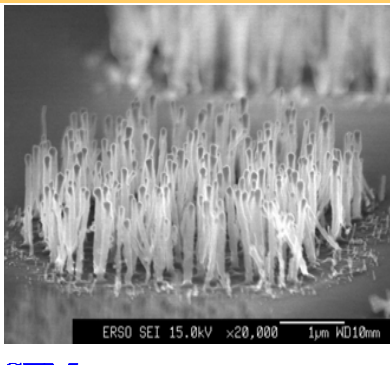
Carbon Nanotube Growth Mechanisms

Base Growth

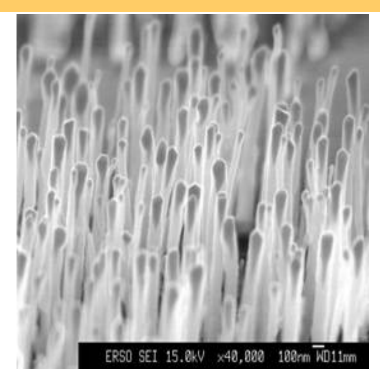
Tip Growth

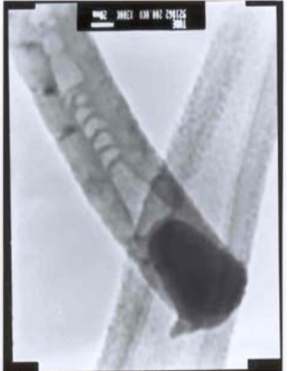


SEM



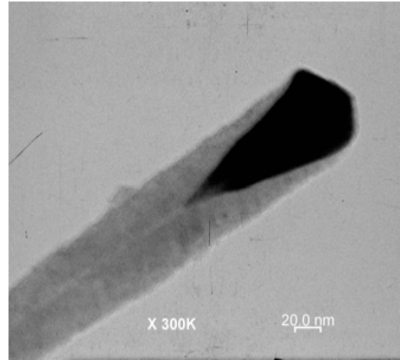
SEM



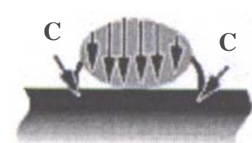


TEM
bamboo-like structure

carbon film cap on top and carbon source at bottom



TEM
hollow tube structure

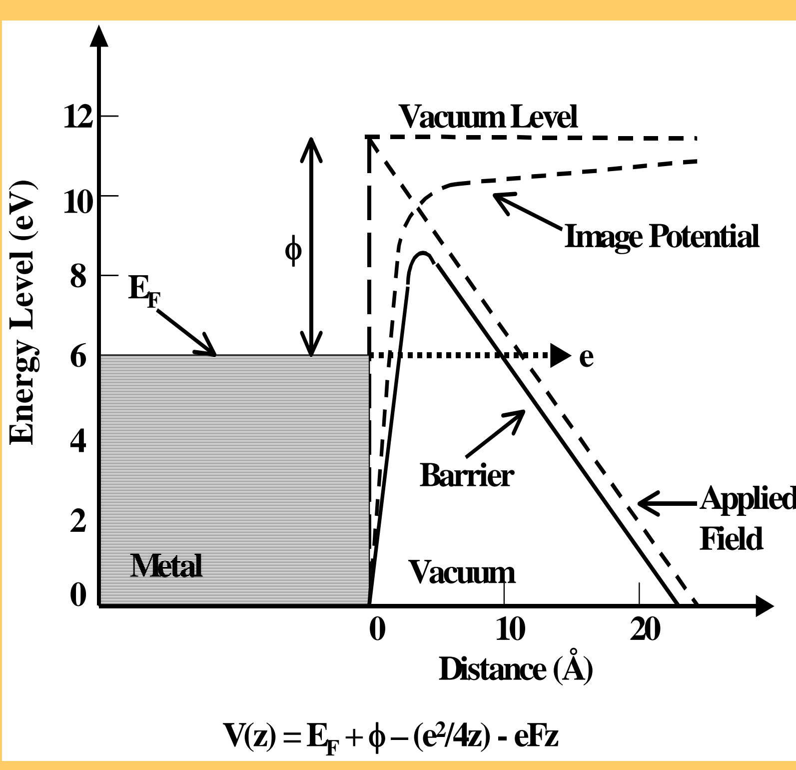


etching at top and carbon source at top

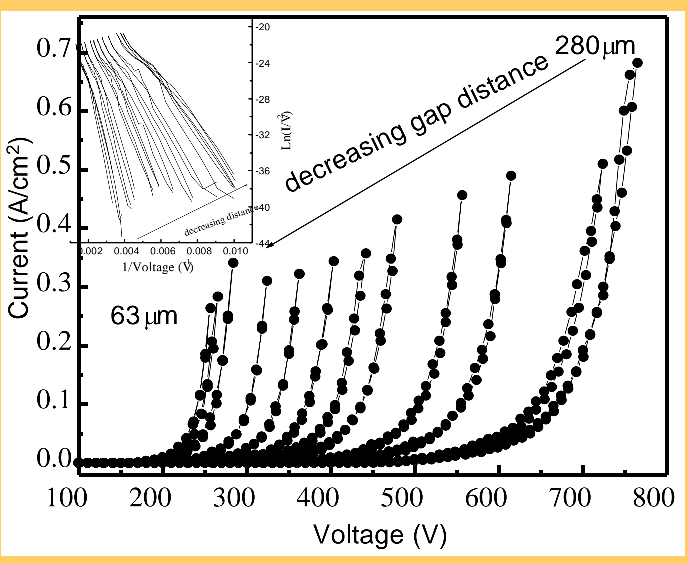
Thermal CVD

ICP-CVD

Field Emission of Carbon Nanotubes



Electrons quantum mechanically tunnel across the barrier Fowler, R. H. and Nordheim, L. W., ***Proc. R. Soc. London A* 119**, 173 (1928).



W.A.de Heer, A. Chatelain, and D. Ugarte, ***Science* 270**, 1179 (1995).

$$I = a\frac{V^2}{\phi}\exp\left(-b\phi^{3/2}/\beta V\right)$$

$$l_n\left(J/E^2\right) \approx a' - \frac{b'\phi^{3/2}}{\beta E}$$

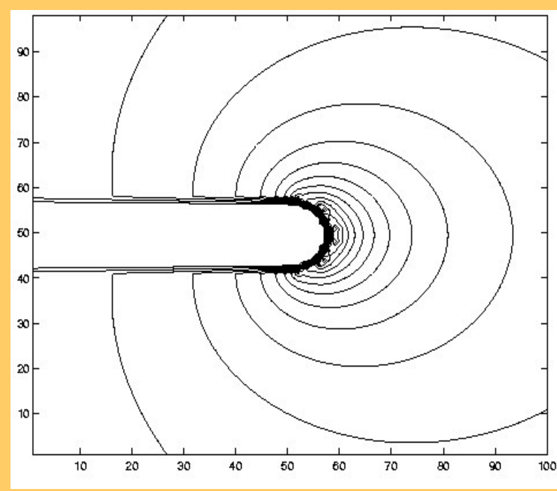
ϕ : work function

β : field enhancemen t factor

Work Function for Electron Emission from CNTs

Type of CNT	Diameter (nm)	Measurement Method	Work Function (eV)	Reference
SWNT	1.0～1.4	Energy Spectrum of Photoelectrons	**4.65 ± 0.1**	Liu X et al., AIP conf. Proc. Vol. 544, 288 (2000)
SWNT	1.4	Energy Spectrum of Photoelectrons	**4.8**	Suzuki S et al., APL 76, 4007 (2000)
SWNT	1.4	Fowler-Nordheim and measured I-V	**5.1**	Bonard J-M et al., APL 73, 918 (1998)
SWNT		Fowler-Nordheim and measured I-V (field emission microscopy)	**4.76～4.88**	Sun JP et al., Appl. Phys. A 75, 479 (2002)
SWNT (armchair)	0.8～8.15	First principle calculation	**6.75～7.05**	Zhou G et al., APL 79, 836 (2001)
MWNT	14～55 (single)	Fowler-Nordheim and measured I-V (in-situ TEM)	**4.6～4.8 (some～5.6)**	Gao R et al., APL 78, 1757 (2001)
MWNT	44	Fowler-Nordheim and measured I-V	**7.3 ± 0.7**	Fransen MJ et al., Appl. Surf. Sci. 146, 312 (1999)
MWNT		Energy Spectrum of Photoelectrons	**5.7**	Chen P et al., PRL 82, 2548 (1999)
MWNT		Energy Spectrum of Photoelectrons	**4.3**	Ago H et al., Phys. Chem. B 103, 8116 (1999)
MWNT	10	Energy Spectrum of Photoelectrons	**4.95**	Shiraishi M. et al., AIP Conf. Proc. Vol. 544, 359 (2000)

Field Enhancement Factor



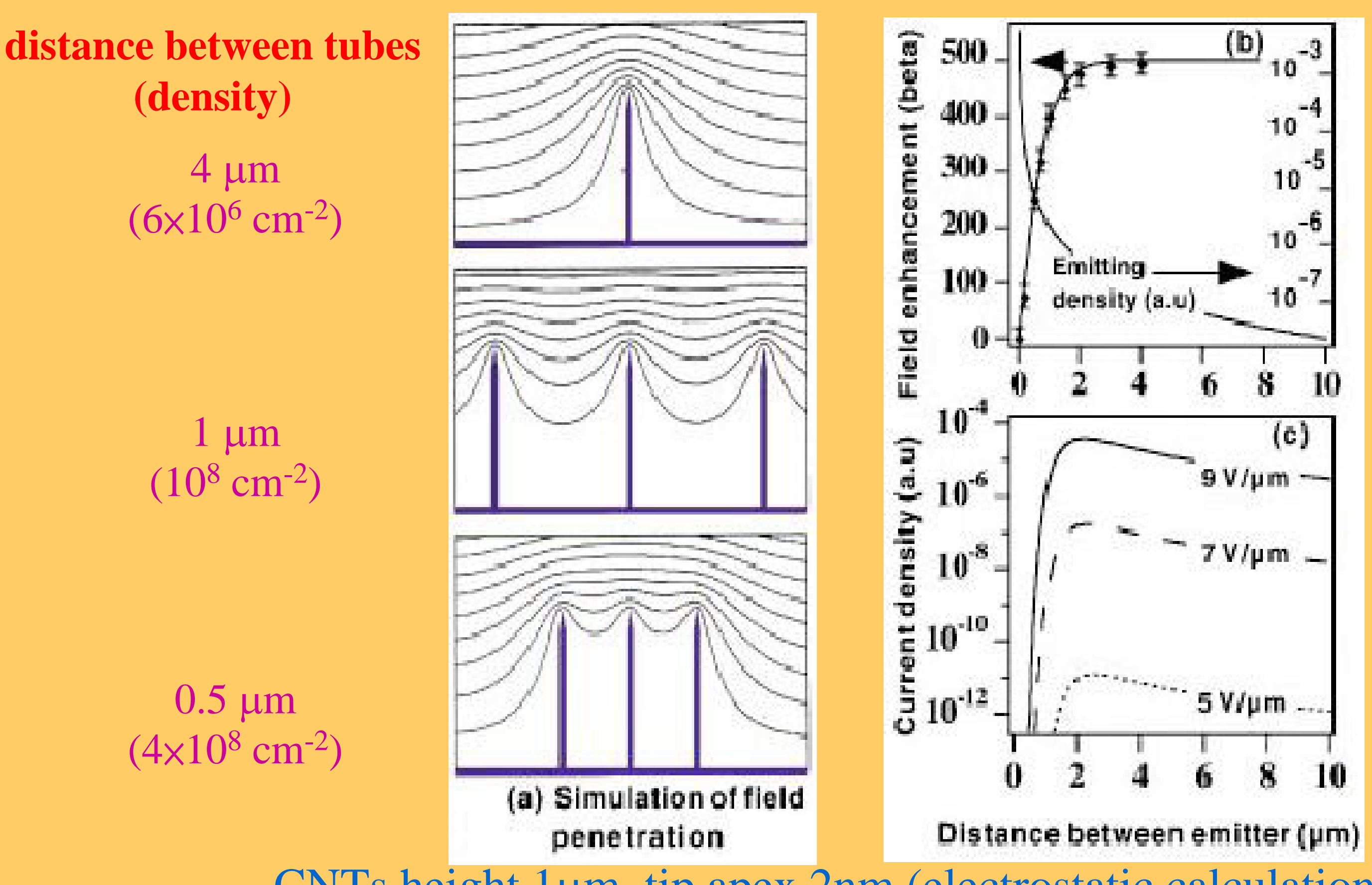
- Electron emission is driven by the local electrical field strength
- The electrical field strength in the vicinity of a nanotube is hundreds times higher than the volumetrically averaged value V/d

- Main features affecting the field emission characteristics:

  ∗ Microstructure / Physical property:
    - SWNT or MWNT
    - electrical conductivity
    - good graphitic structure

  ∗ Geometrical features:
    - aligned or non-aligned
    - closed or open-ended
    - tip curvature
    - diameter and length (aspect ratio)
    - density

CNT Field Emission of Different Densities



CNTs height 1µm, tip apex 2nm (electrostatic calculation)

L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J-M. Bonard and K. Kern, ***Appl. Phys. Lett.* 76**, 2071 (2000).

Process Modification for Field Enhancement

- Plasma Pre-treatment

catalyst

Substrate

catalyst deposition

plasma treatment

Ar ion

annealing / etching pretreatment

catalyst density reduction

CVD growth

Control of Nanocatalyst Size / Density by Ar Sputtering

Pretreatment: ICP CVD

Parameters	
Gas	Ar: 10sccm
Pressure	40mTorr
RF Power	1000 W
Time	2, 5, 10 min
Bias	-400V

CNTs Growth: ICP CVD

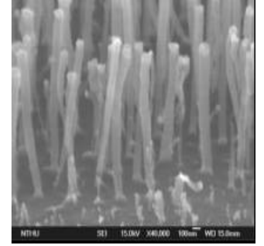
Parameters	
Gas	C_2H_2 : 10sccm H_2 : 20sccm
Pressure	17mTorr
RF Power	1000 W
Time	10 min

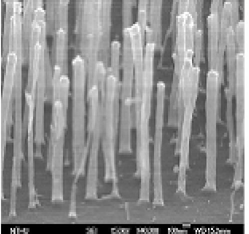
Catalyst: Electron Gun

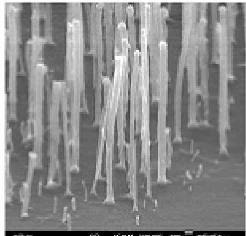
Ni 100 A

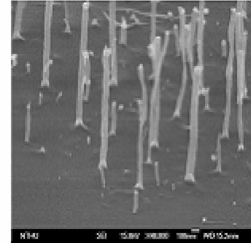
Sisubstrate

No Sputtering	2 min	5 min	10 min









With Ar plasma sputtering under –400 V bias for 10 min, the catalyst particle density was obviously reduced.

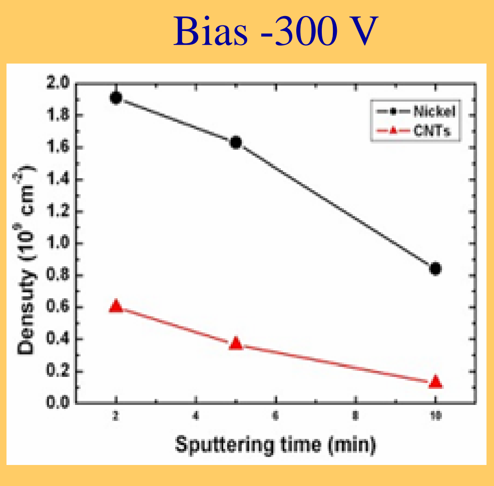
CNT density was drastically reduced for those pretreated under –400 V bias consistent with the change of particle density, and good vertical alignment was kept even at low density ($\sim 10^8$ cm^{-2}).

C.T. Lin et al, *9th International Conference on New Diamond Science and Technology (ICNDST-9) Mar. 26-29, 2004, Tokyo, Japan.*

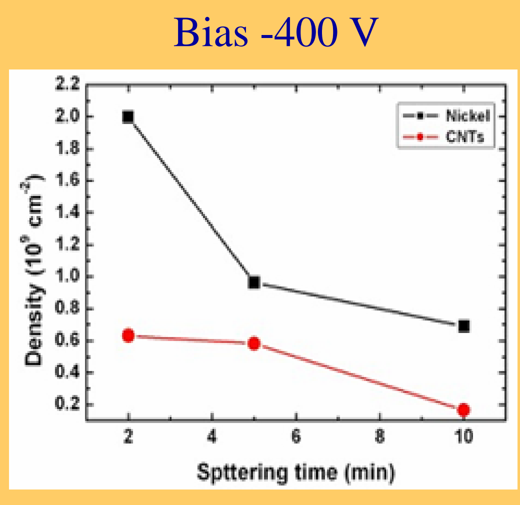
Effects of Ar Sputtering on CNT Density and Field Emission

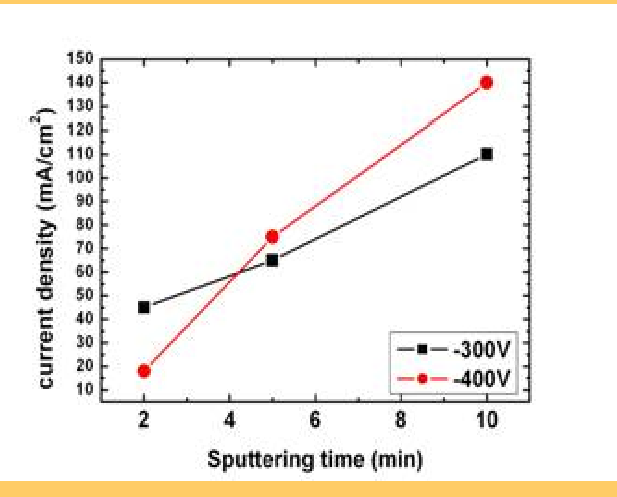
Ar plasma sputtering, ICP power 1000 W
Ar flow rate 10 sccm, pressure 40 mTorr

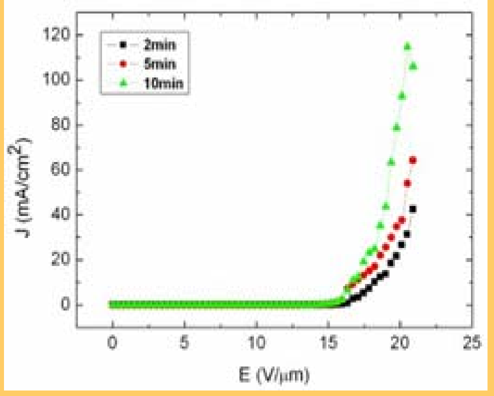
Bias -300 V

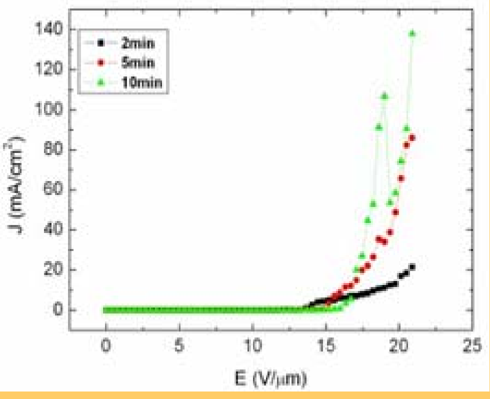


Bias -400 V







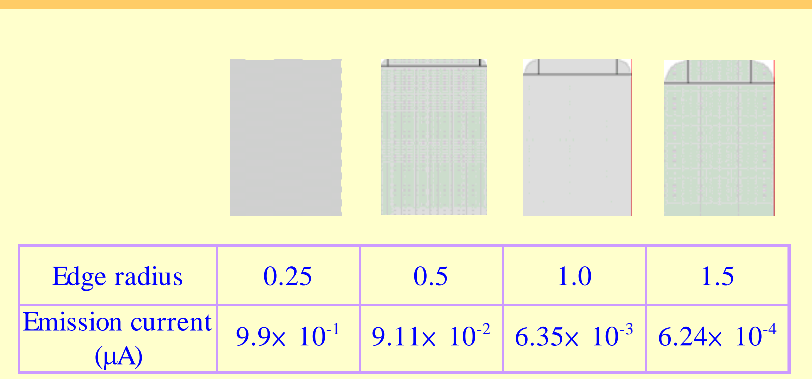


C.T. Lin et al, *9th International Conference on New Diamond Science and Technology (ICNDST-9) Mar. 26-29, 2004, Tokyo, Japan.*

Field Emission from a Single MWNT (simulation)

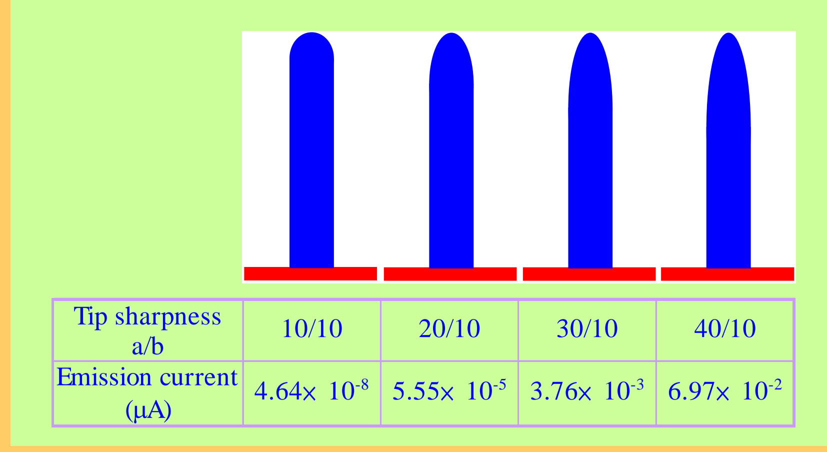
Applied voltage 40V, cathode-to-anode distance 2μm
MWNT height 100nm, radius 10nm, work function 1eV

Open-ended
Effect of Edge Sharpness



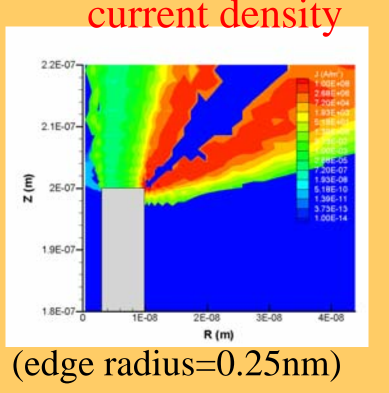
Edge radius	0.25	0.5	1.0	1.5
Emission current (μA)	9.9×10^{-1}	9.11×10^{-2}	6.35×10^{-3}	6.24×10^{-4}

Colsed-caped
Effect of Tip Sharpness

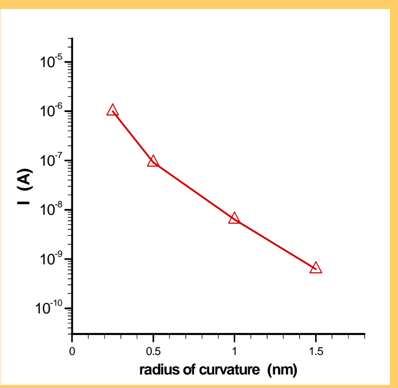


Tip sharpness a/b	10/10	20/10	30/10	40/10
Emission current (μA)	4.64×10^{-8}	5.55×10^{-5}	3.76×10^{-3}	6.97×10^{-2}

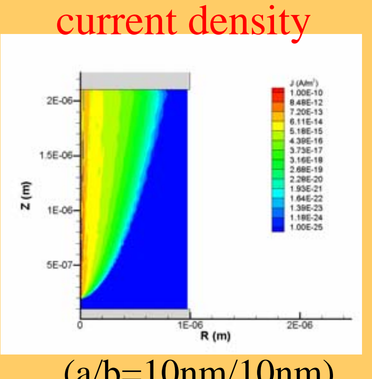
current density



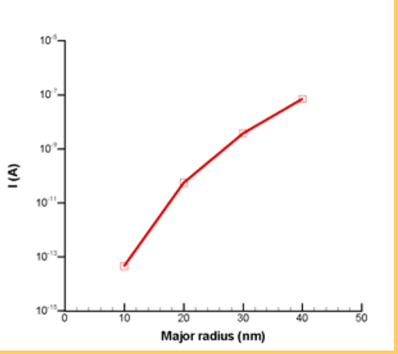
(edge radius=0.25nm)



current density

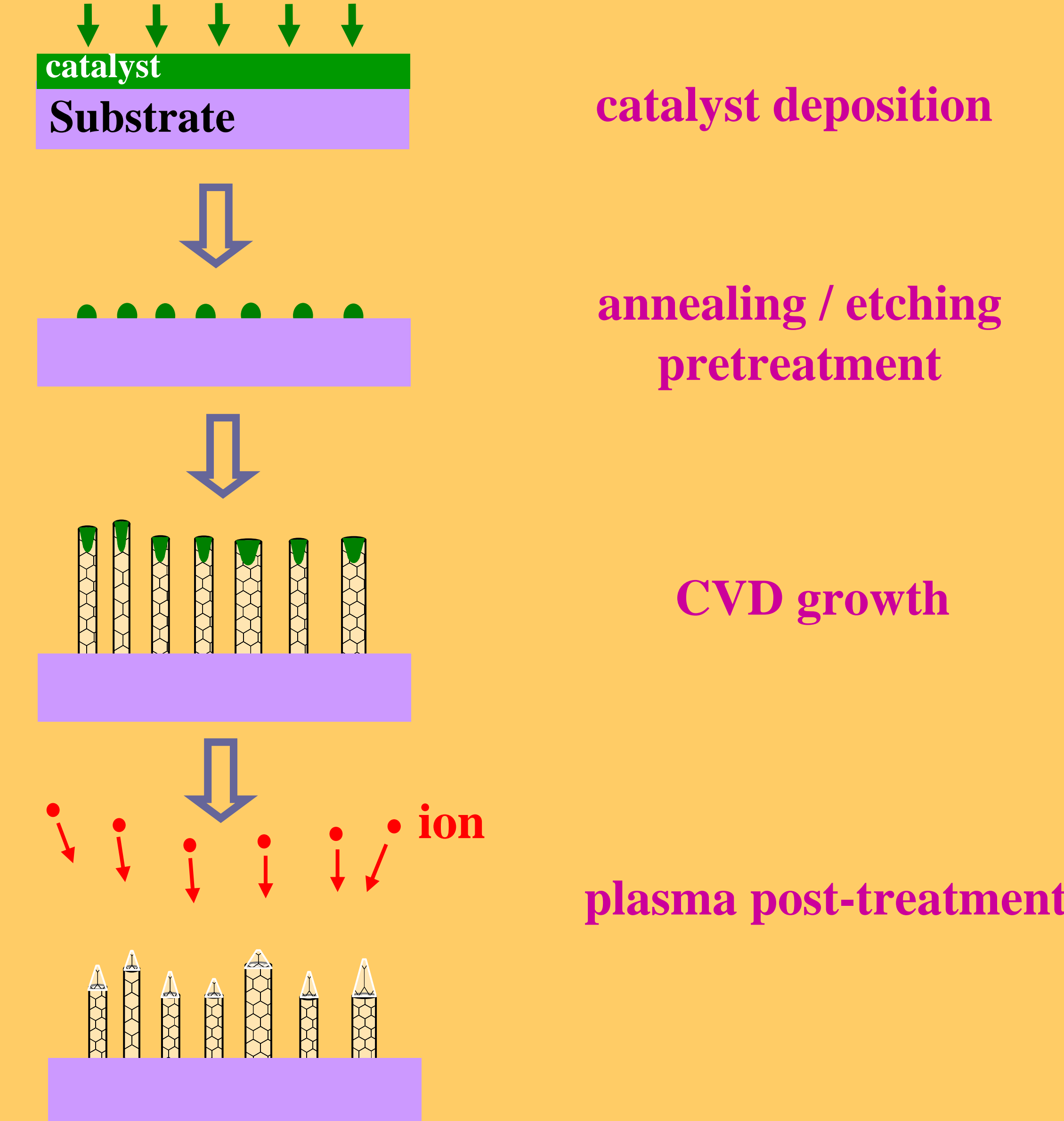


(a/b=10nm/10nm)



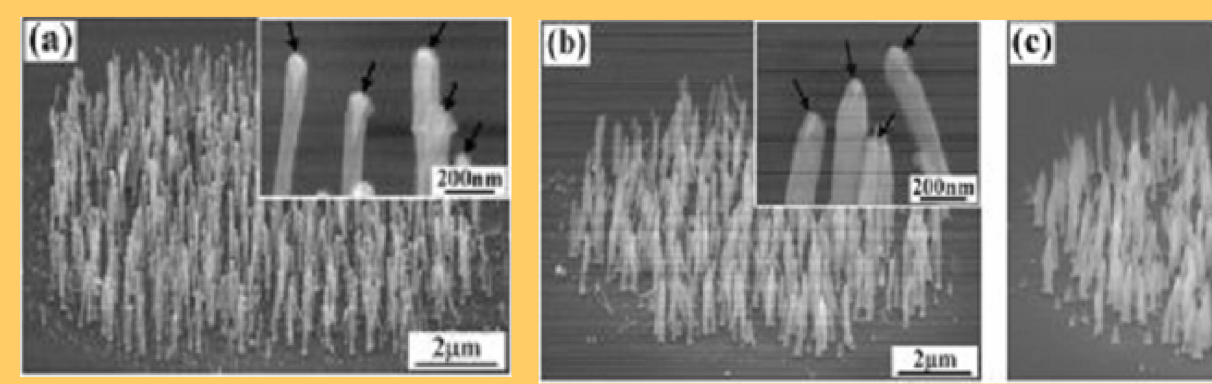
Y. Hu et al. (2002)

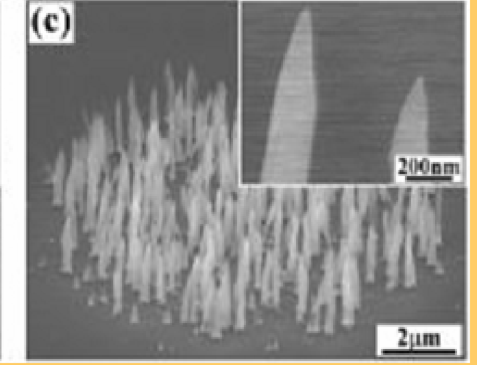
Process Modification for Field Enhancement
- Plasma Post-treatment

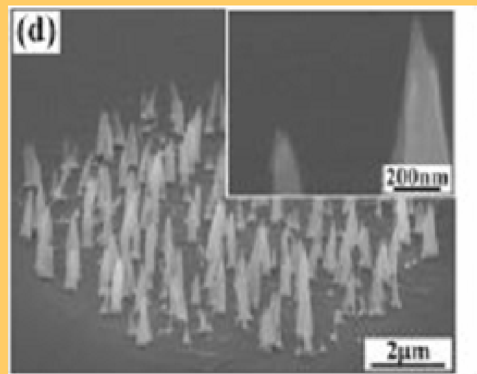


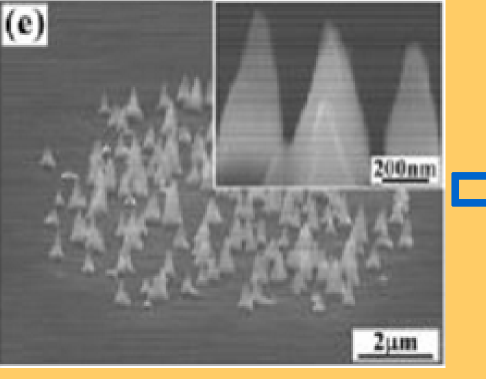
Plasma Post-treatment of ICP-CVD grown CNTs

Ar plasma sputtering, ICP power 1000 W
RF bias power 300 W, pressure 20 mTorr





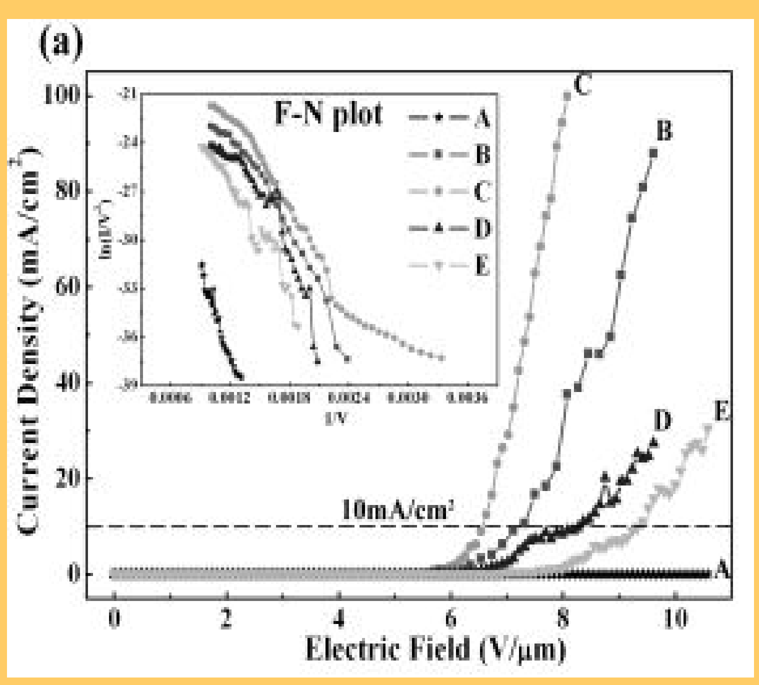


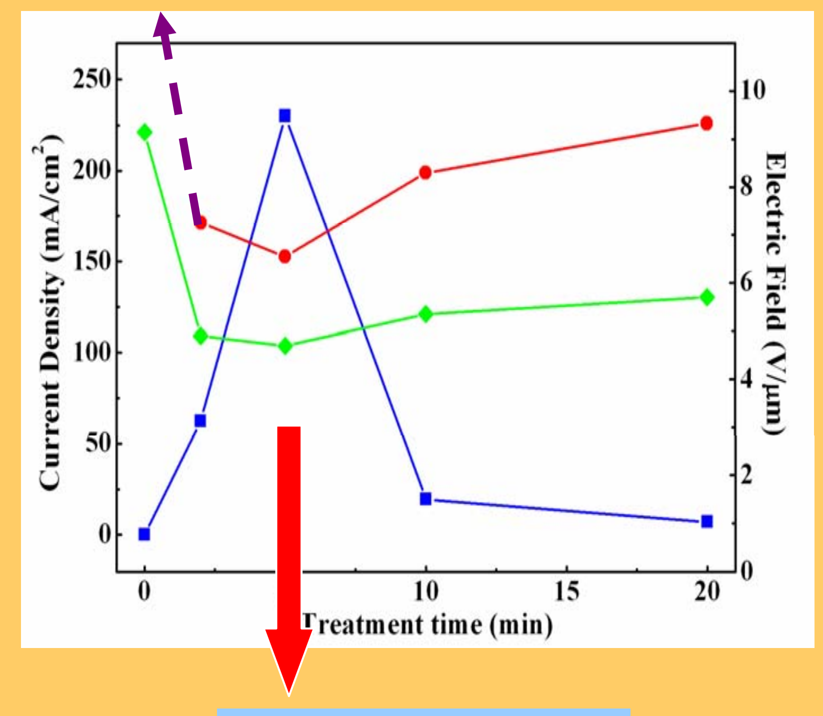


Encapsulated Ni nanoparticles at CNTs tips were gradually removed after 5 min treatment with Ar plasma and the tips became cone-shaped.

C.H. Weng et al. *Appl. Phys. Lett.* 85, 4732 (2004).

Field Emission Characteristics of CNTs after Plasma Post-treatment

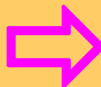




A: as grown B: 2 min C: 5 min
D: 10 min E: 20 min

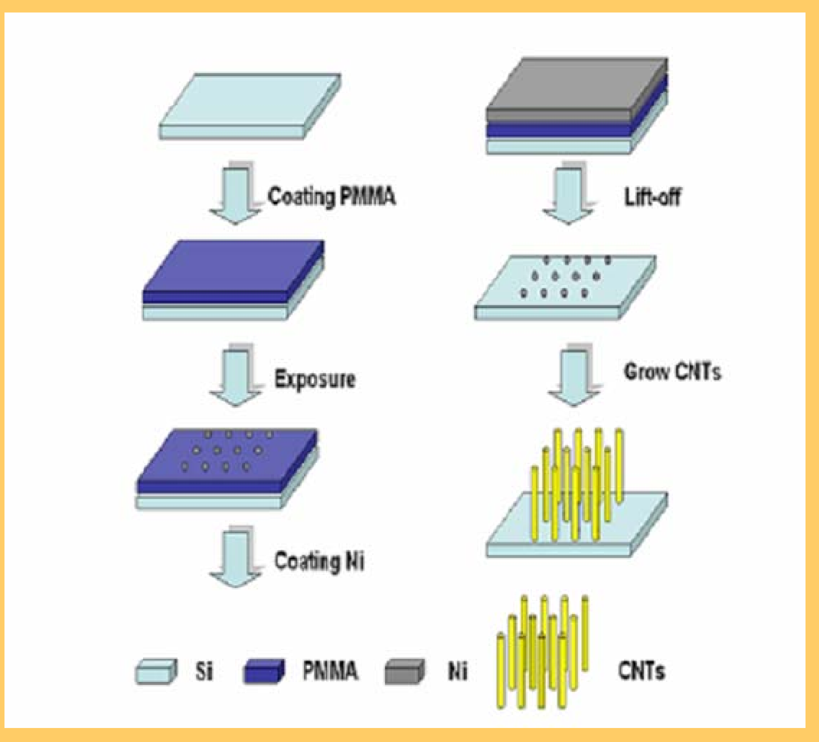
Optimal condition

C.H. Weng et al. *Appl. Phys. Lett.* 85, 4732 (2004).

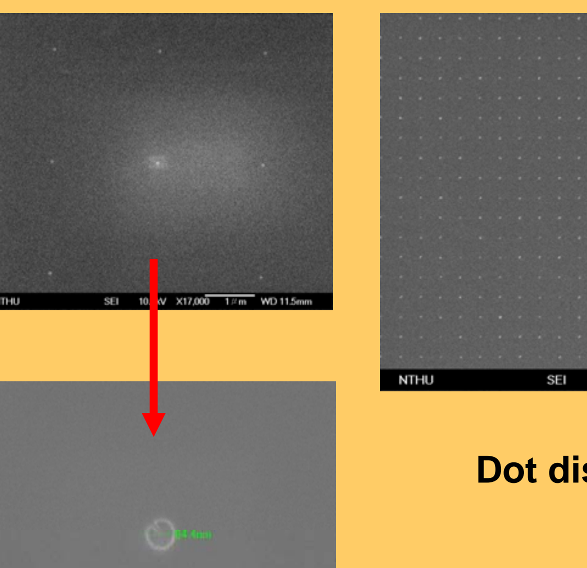
 **Best field emission property at 5 min post-treatment**

Controlled Growth of Single Free-standing MWNT

• **Catalyst Definition by E-Beam Lithography**



After development **After lift-off**

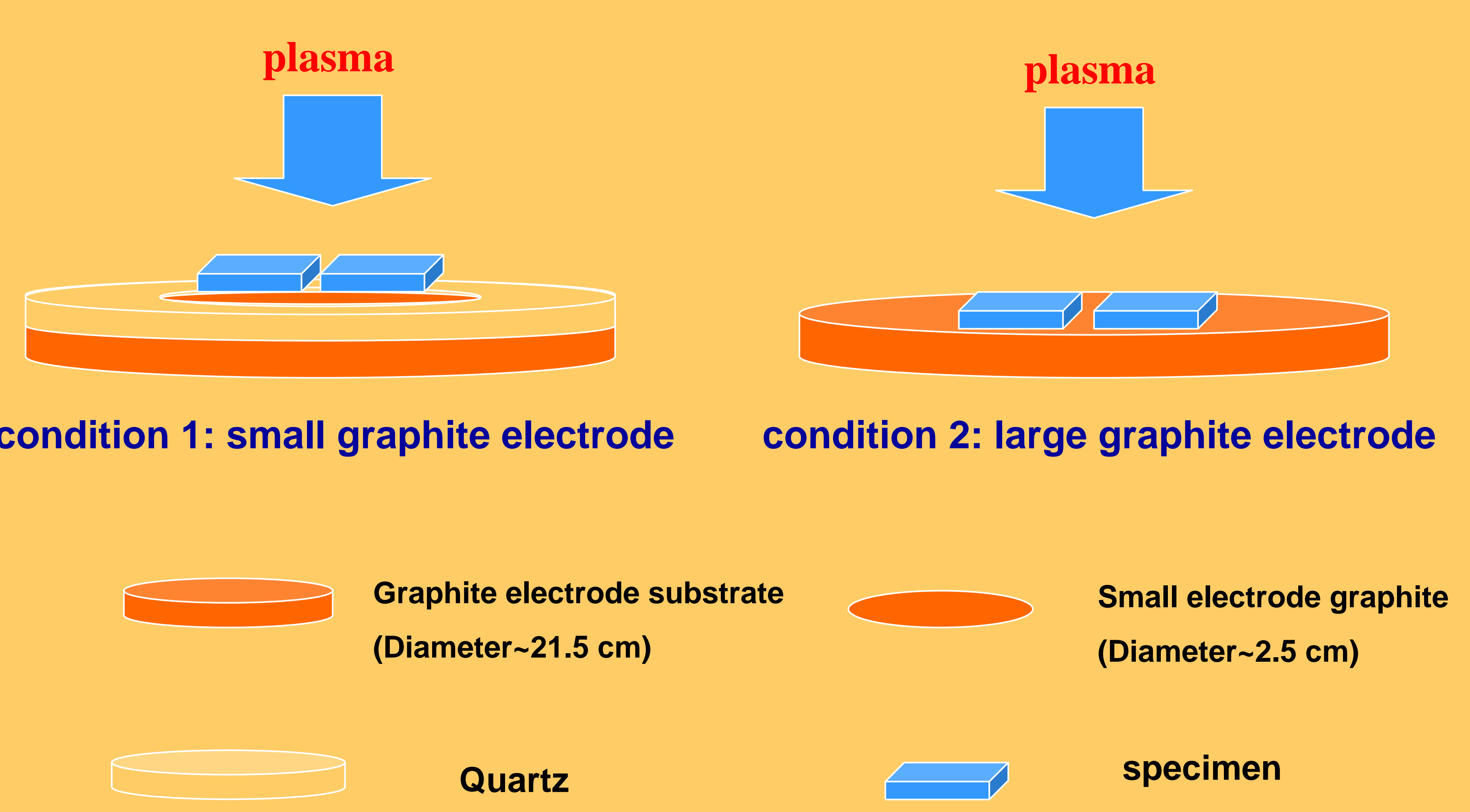


Dot distance 1μm

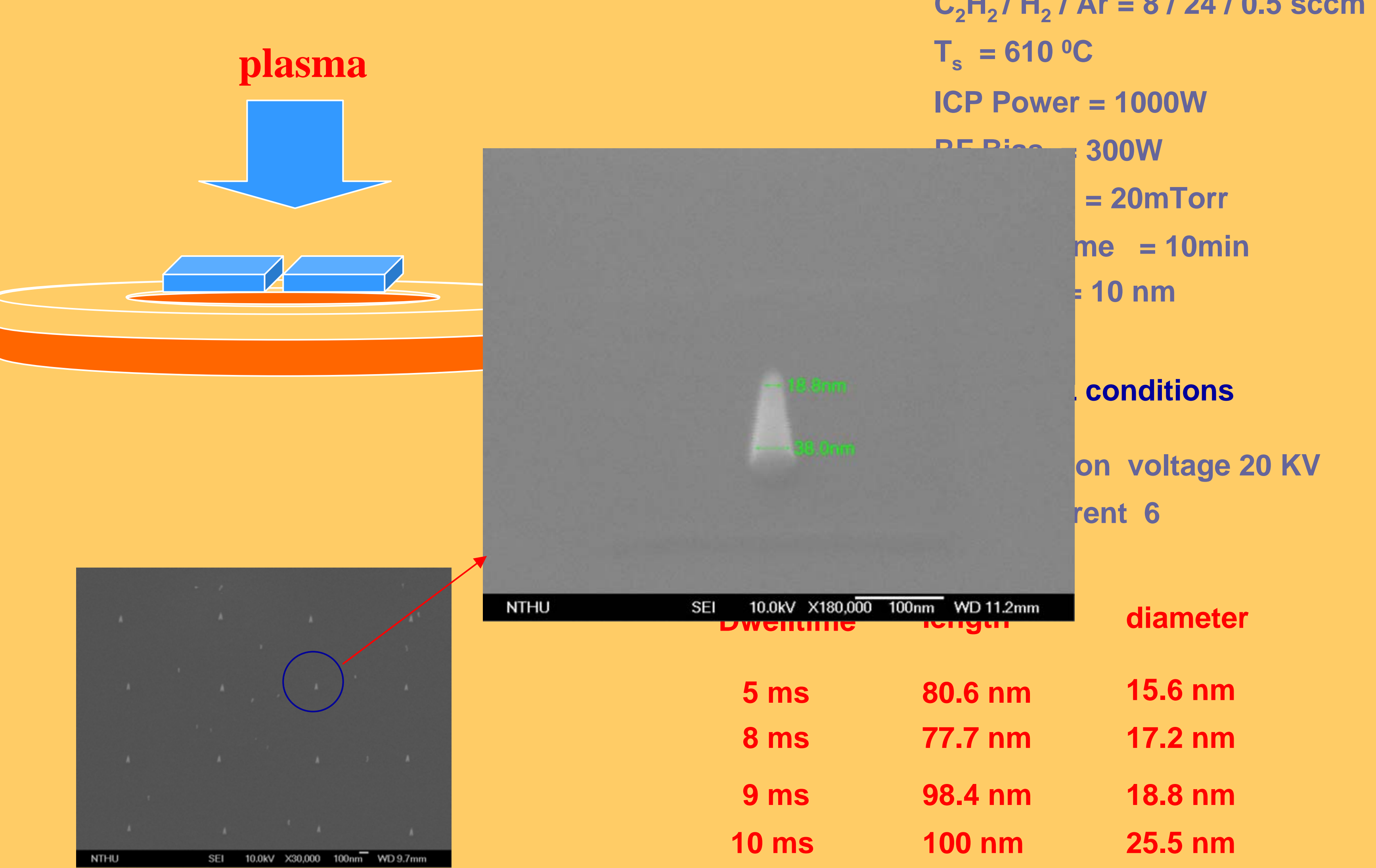
EBL conditions

- **Acceleration voltage 20KV**
- **Probe current 6**
- **Exposure time 8 ms**

CNTs growth with different substrates by ICP-CVD



condition 1: small graphite electrode



ICP Conditions

C_2H_2 / H_2 / Ar = 8 / 24 / 0.5 sccm

T_s = 610 ^{0}C

ICP Power = 1000W

= 300W

= 20mTorr

me = 10min

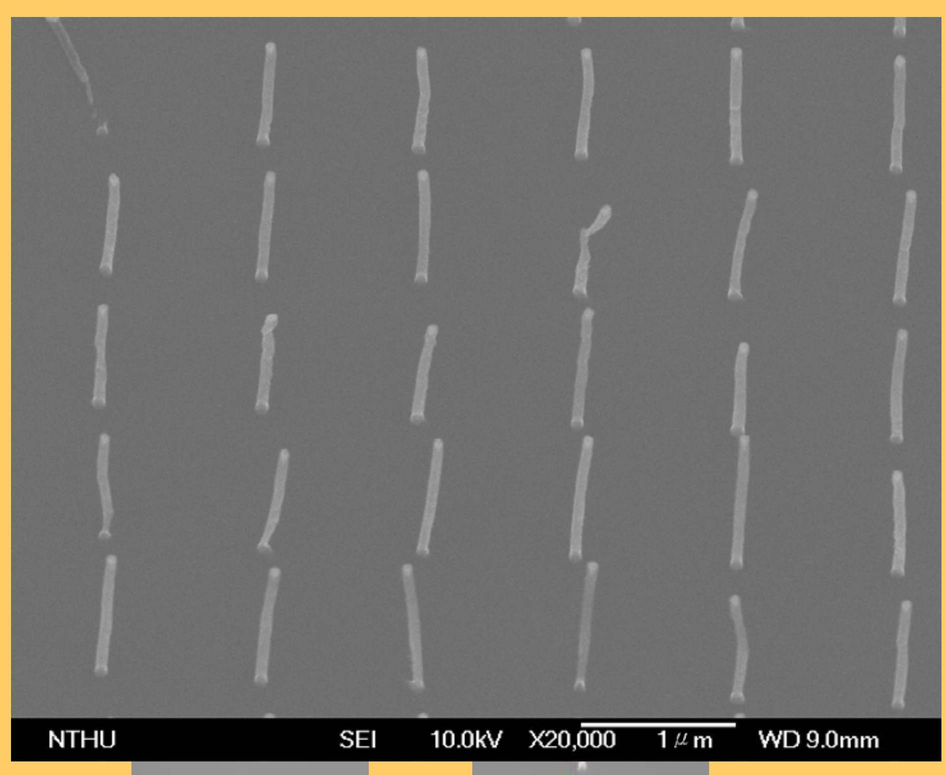
= 10 nm

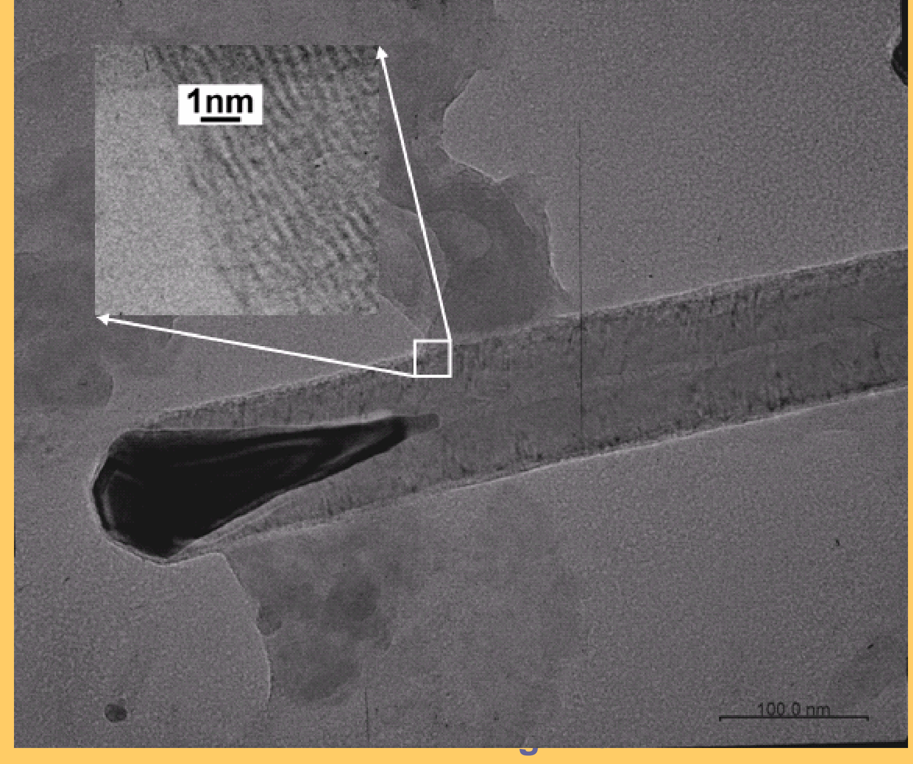
conditions

on voltage 20 KV

rent 6

		diameter
5 ms	80.6 nm	15.6 nm
8 ms	77.7 nm	17.2 nm
9 ms	98.4 nm	18.8 nm
10 ms	100 nm	25.5 nm





Dwelltime 5ms

Dwelltime 8ms

Dwelltime 6ms

Dwelltime 9ms

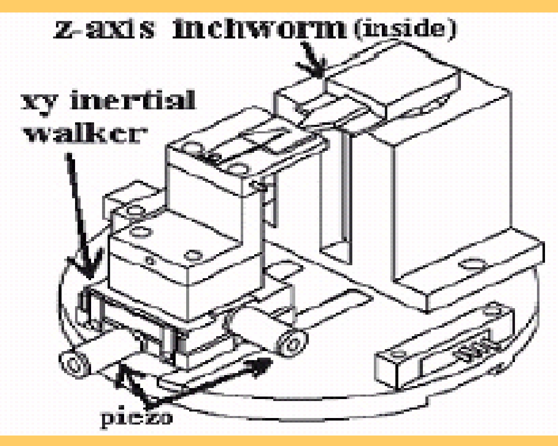
Dwelltime 7ms

Dwelltime 10ms

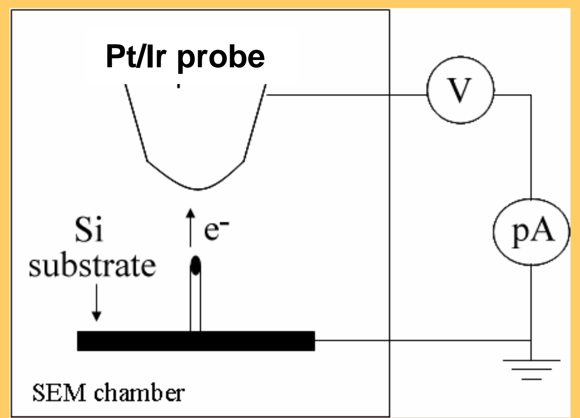
Probe current 6

Dwelltime	length	diameter
5 ms	453 nm	31.1 nm
6 ms	552 nm	34.4 nm
7 ms	709 nm	33.3 nm
8 ms	788 nm	37.5 nm
9 ms	837 nm	41.7 nm
10 ms	800 nm	44.8 nm

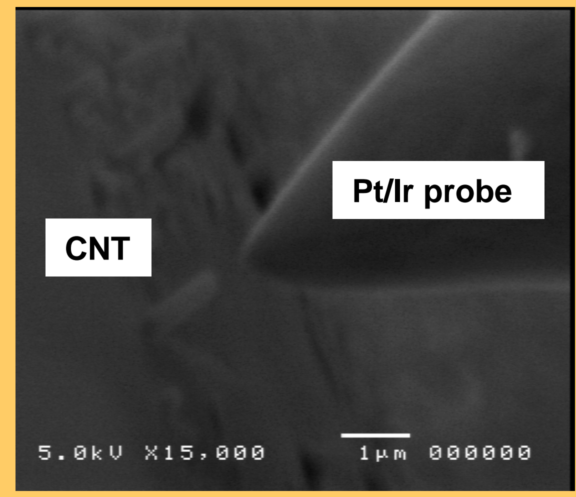
Field emission characterization of single CNT



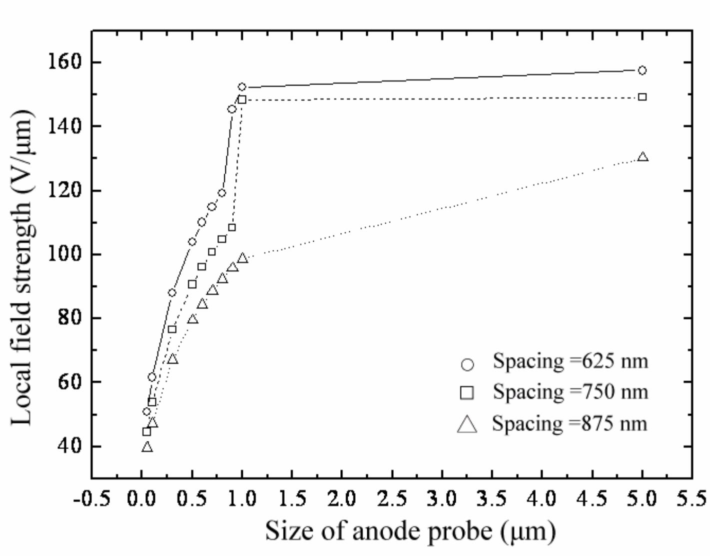
Carbon nano tip ssembler
inertial walker for x- and y-axis.
inchworm unit for z-axis.



Schematic of a probe-type anode diode structure for field emission measurement (title angle of the specimen is ~85^0, and the angle between probe and CNT tip is 135^0)



The image of CNT(cathode) and probe (anode)



Relation between local peak field strength and anode probe size

Code : SIMION 7.0
Length of CNT : 800 nm
Diameter of CNT : 50 nm
Anode voltage : 12 V

As the diameter of anode probe is higher than 1 μm, the local peak field strength is equal to a planar anode.

Field emission characteristics of single CNT

I-V emission characteristic of single VACNT as a function of the spacing between CNT and Pt/Ir probe

Conical CNT

Current (nA)

Voltage (V)

tip-tube spacing

625 nm

750 nm

875 nm

Tubular CNT

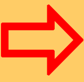
Current (nA)

Voltage (V)

tip-tube spacing

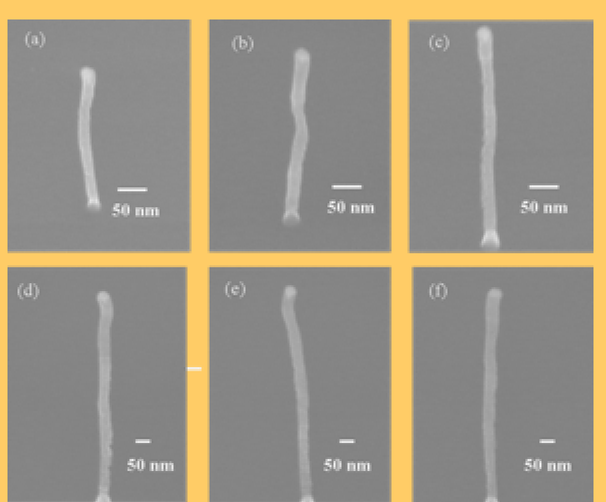
500 nm

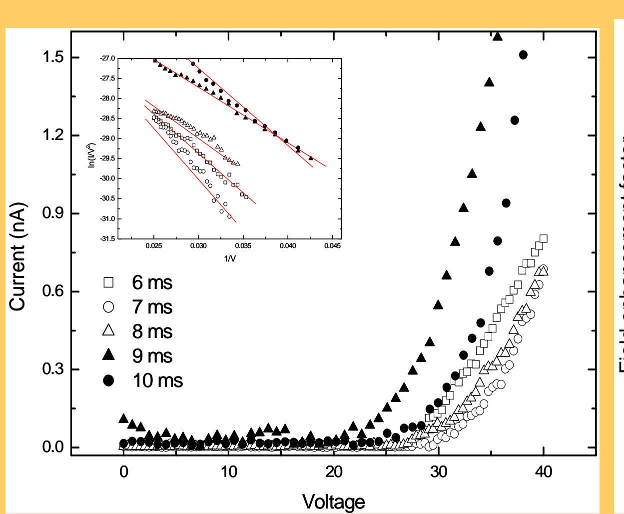
1000 nm

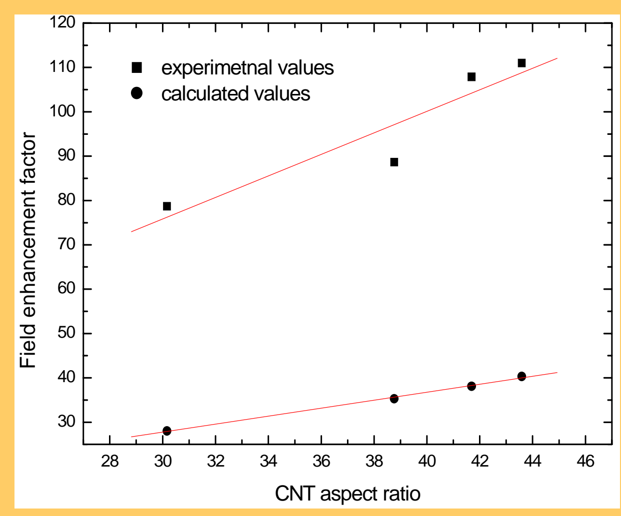


- Results of Field emission measurement on single CNTs revealed Fowler-Nordheim characteristics.
- The field enhancement factor increases with the anode-CNT spacing.

Field emission characteristics of single CNT







Dwell times (ms)	radius (nm)	CNT length (nm)	aspect ratio	experimental values (β)	calculated* values (β)
6	18.3	552	30.16	78.71	28.04
7	18.35	709	38.76	88.66	35.32
8	18.9	788	41.69	107.89	38.12
9	19.2	837	43.59	110.99	40.34

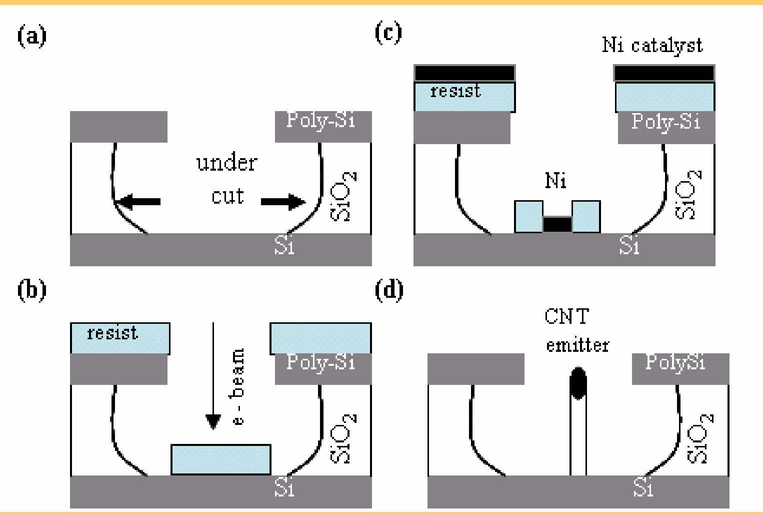
*Theoretical calculation:

$$\beta = 1.2\left[2.5+\frac{h}{r}\right]^{0.9}\left[1+0.013\left(\frac{d-h}{d}\right)\right]^{-1} - 0.033\left(\frac{d-h}{d}\right)$$

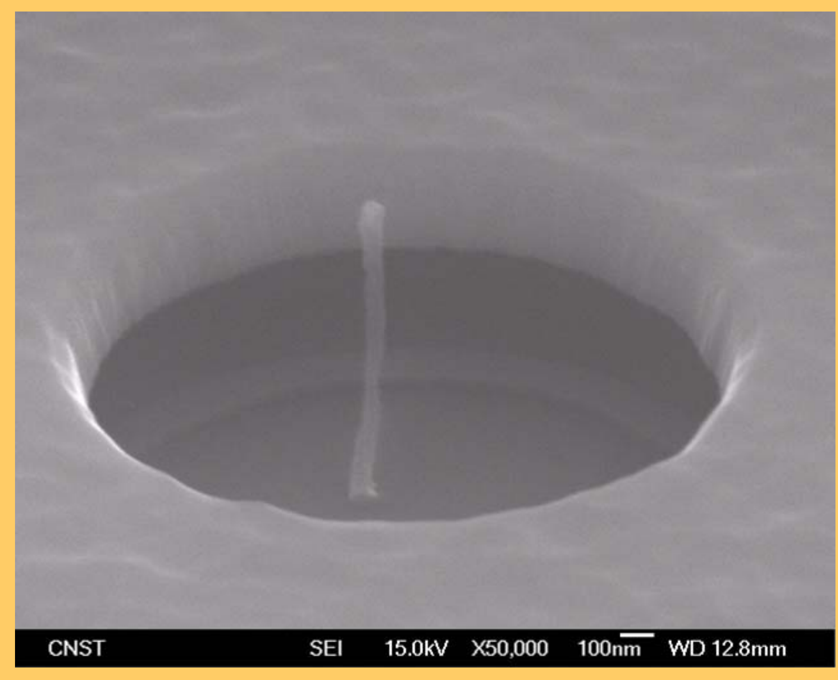
J. M. Bonard, etc. ***Phy.Rev.Lett.* 89,** 197602 (2002).

- **The field enhancement factors of CNTs increased with the tube aspect ratio.**
- **However, the experimental values were 2~3 times higher than the theoretical alculations based on literature, which needs further investigation.**

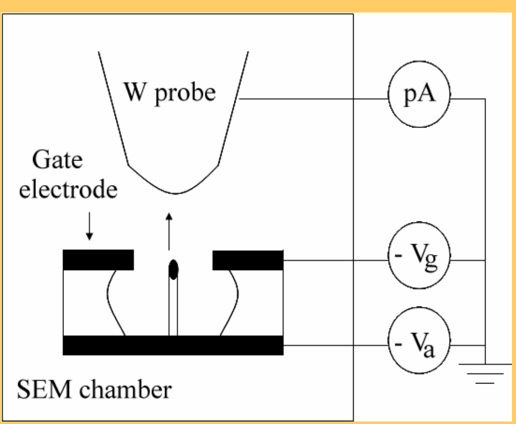
Triode structure device with single CNT



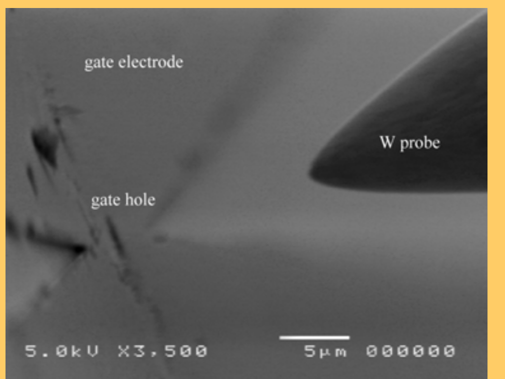
Process for fabricating CNT microcathode gated structure: (a) Deposition of SiO2 insulator and poly-Si electrode, followed by optical lithography and etching, (b) Resist (PMMA) coating and E-beam lithography, (c) Sputter deposition of Ni catalyst, and (d) Lift off and CNT growth by ICP-CVD.



Gated CNT structure with a 800 nm height and 54 nm diameter nanotube (gate hole size = 1.5 μm)



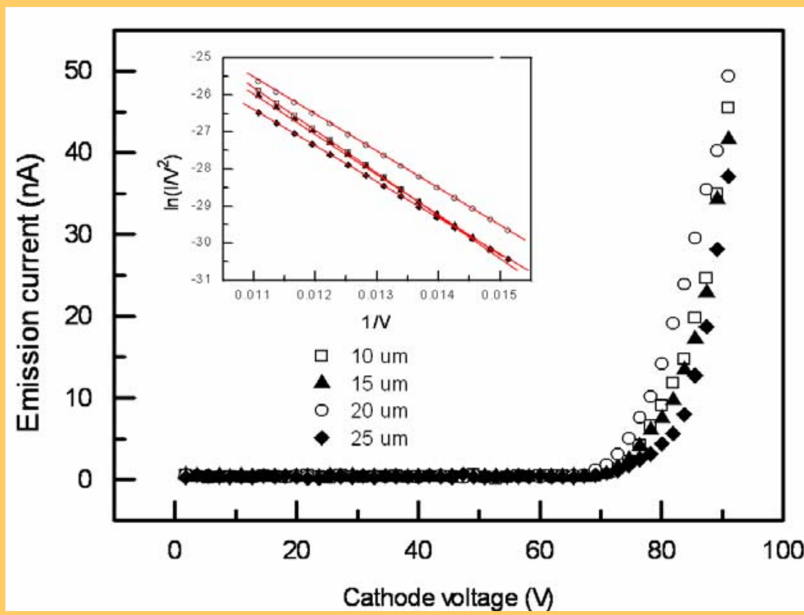
Schematics of the field emission measurement system used to examine a single gated device.



SEM images of spacing between CNT and gate electrode. The spacing is about 10 μm.

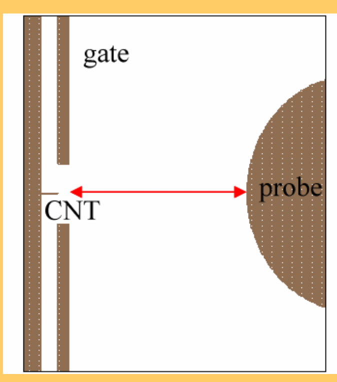
S.C. Tseng et al. *Diamond and Related Materials,* 14 (2005) 2064.

The relation between the gate electrode-to-probe spacing and field emission characteristics

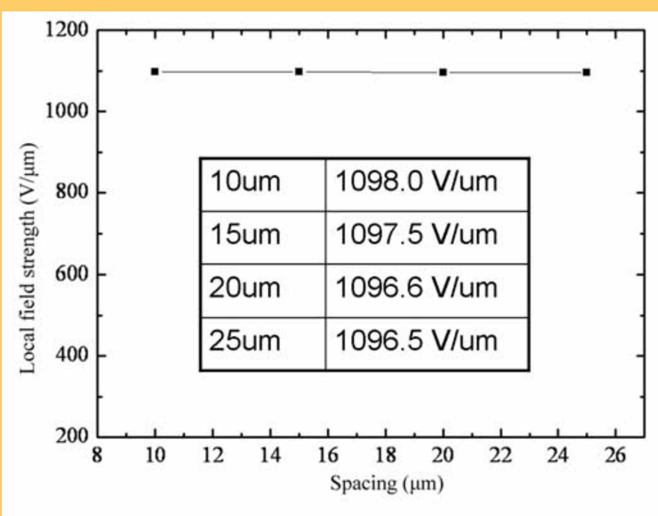


I-V emission characteristics with different spacing between anode-to-gate.

The gate size is 1.5 μm; height of CNT is 530 nm. The inset shows the data plotted in Fowler-Nordheim form.



To simulate the relation between spacing (gate electrode-to-probe) and local filed strength at the apex of CNT.
Simulation conditions:
Aperture size : 1.5 μm ; The height of the CNT : ~530 nm
The voltage of the gate : -10 V ;
The voltage of the probe : 0 V

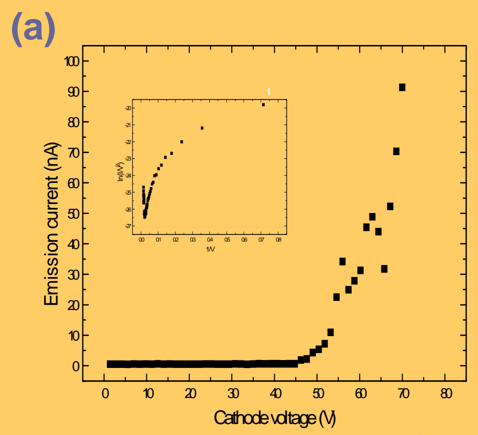


Spacing	Local field strength
10um	1098.0 V/um
15um	1097.5 V/um
20um	1096.6 V/um
25um	1096.5 V/um

The relation between spacing (gate electrode-to-probe) and local field strength at the apex of CNT (Simulation by Simion 7.0)

Field emission characteristics with different control scheme

(a)



(b)

Emission current (nA)
Gate voltage (V)

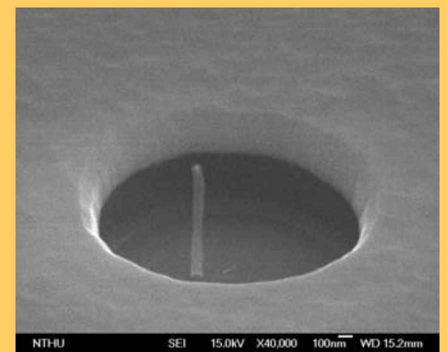
(c)

Emission current (nA)
Gate voltage (V)

(a) constant gate voltage (-10 V) and scanning cathode voltage (0~ -70 V). (b) scanning gate voltage (-45 V~45 V) and constant cathode voltage (–50 V). (c) scanning gate voltage (-50 V~50 V) and constant cathode voltage (–60 V). (d) combine (a)~(c) into one figure.

(d)

Emission current (nA)
Potential difference (V)
ln(I/V²)
1/V
-60V/-50V~50V
-50V/-45V~45V
-70V/-10V

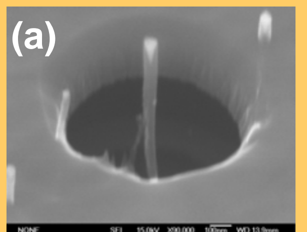


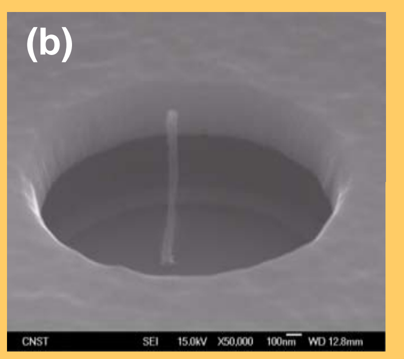
Aperture size : 2.0 μm

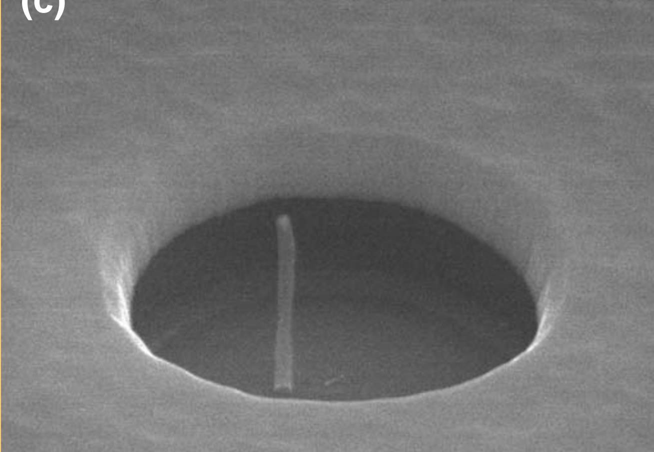
The height of the CNT : ~800 nm

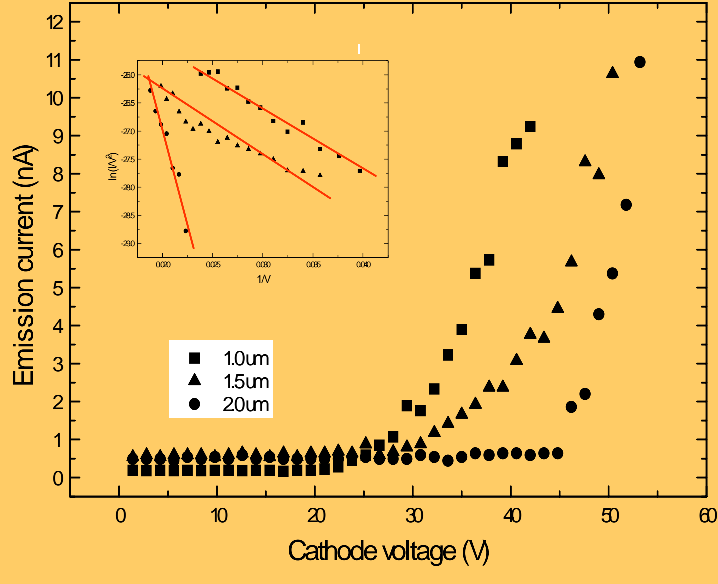
Field emission characteristics with various gate hole size

CNT gated structure with different hole size of gate (a) 1.0 μm (b) 1.5 μm (c) 2.0 μm . The height of single vertically aligned CNT is about 800 nm.

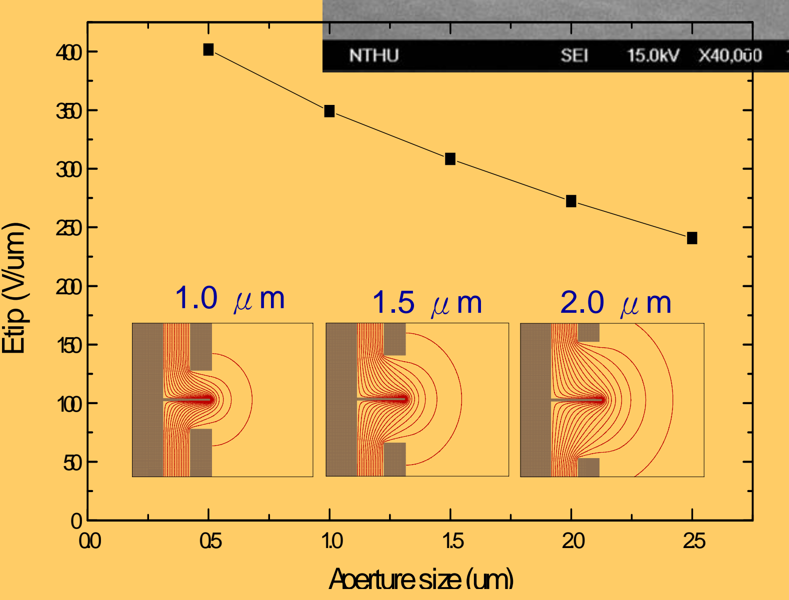








I-V emission characteristics with different gate hole size. The inset shows the data plotted in Fowler-Nordheim form.

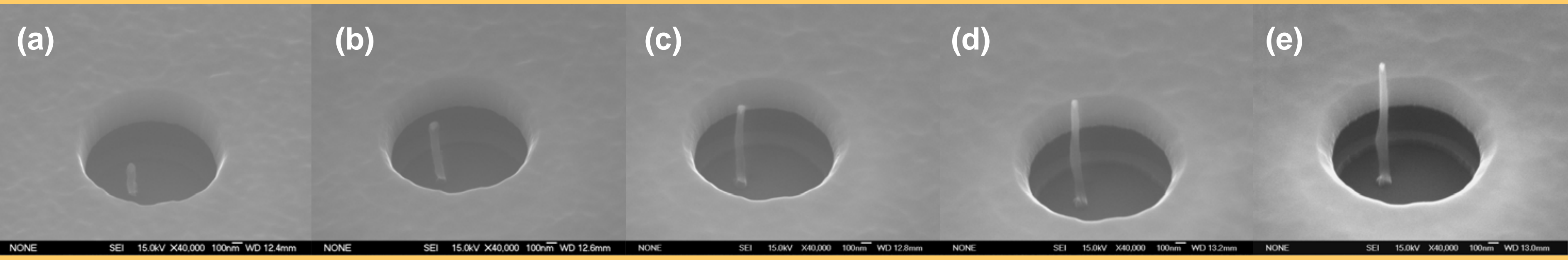


Calculated tip peak field strength (field enhancement) with various gate hole size.

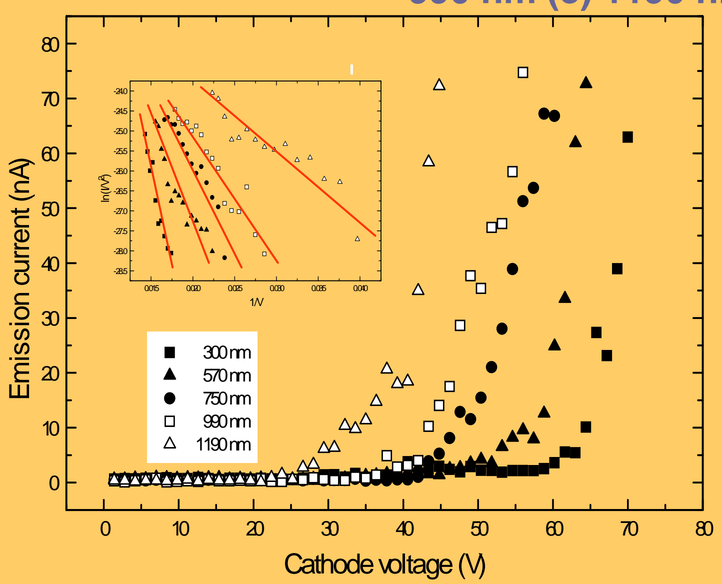
(Simulation by Simion 7.0)

S.C. Tseng et al. *Diamond and Related Materials,* 14 (2005) 2064.

Field emission characteristics with various CNT height

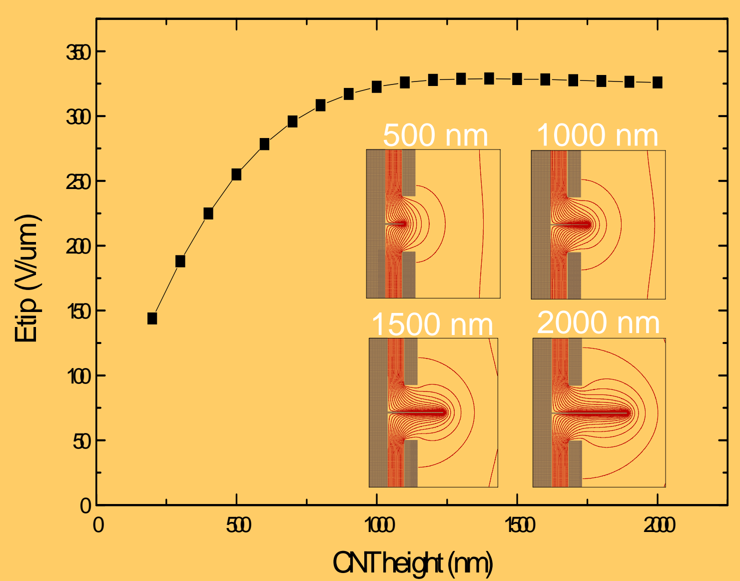


CNT Gated structure with different height of CNT (a) 300 nm (b) 570 nm (c) 750nm (d) 990 nm (e) 1190 nm. The gate hole size is 1.5 μm.



I-V emission characteristics from gate electrode device (gate hole size 1.5 μm) with different height of single vertically aligned CNT. The inset shows the data plotted in Fowler-Nordheim form.

S.C. Tseng et al. submitted to *Nanotechnology*.

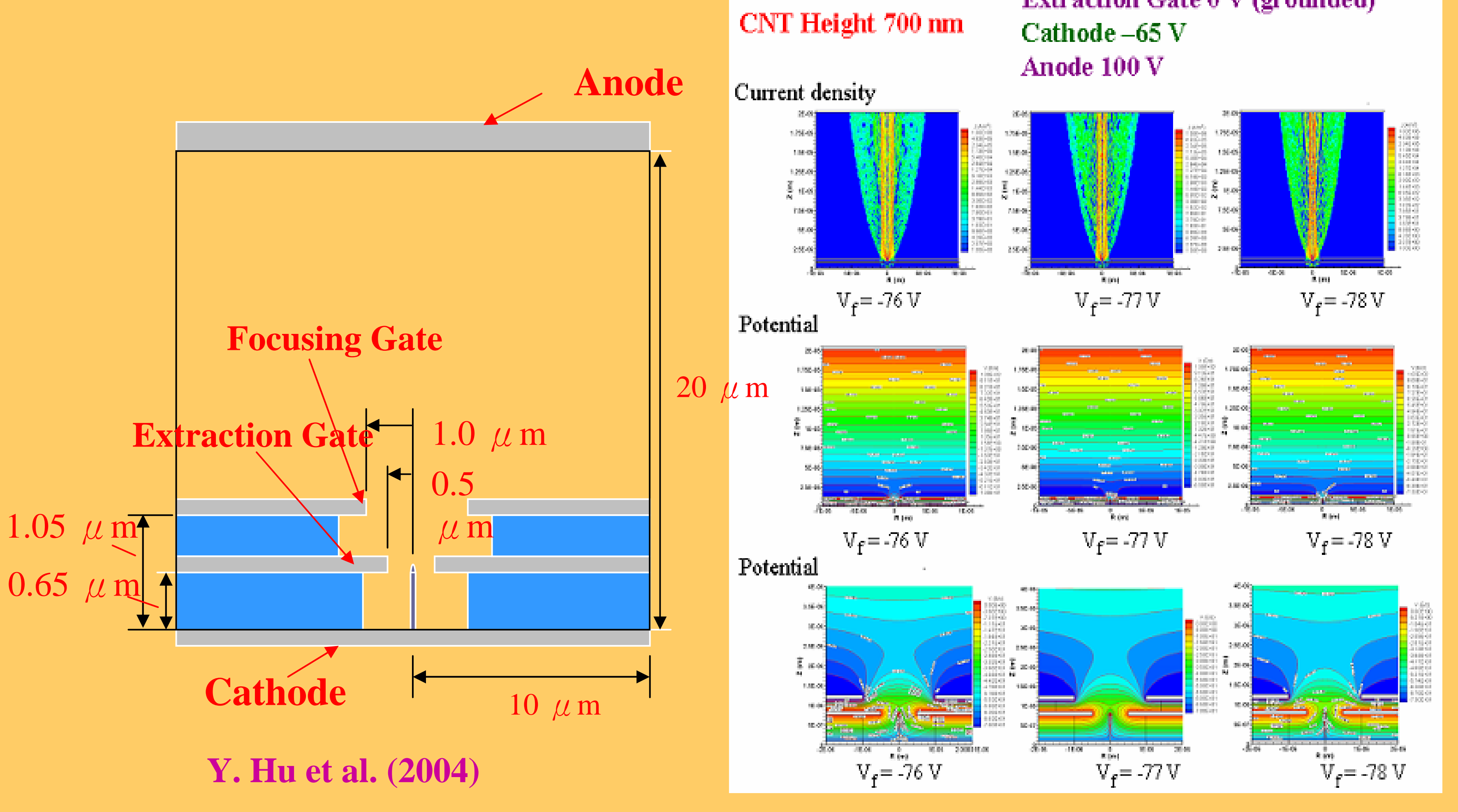


Calculated tip peak field strength (field enhancement) with various CNT height.

(Simulation by Simion 7.0)

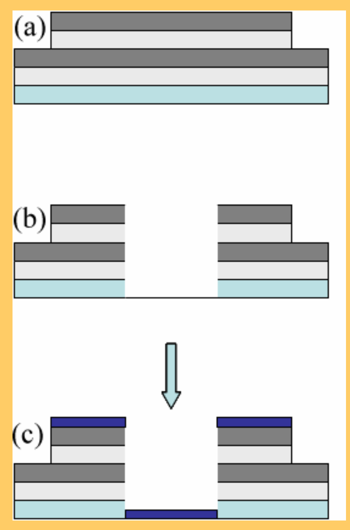
Double-gated Triode Field Emitter Design & Simulation

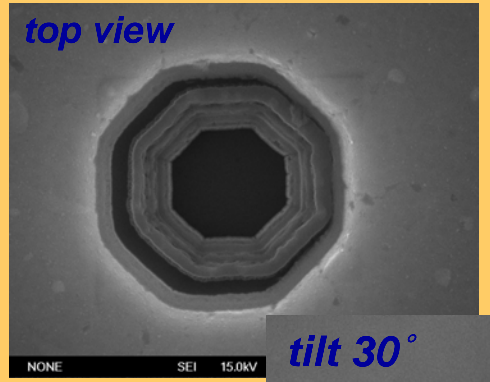
Extraction gate hole radius: 0.5 μm
Focusing gate hole radius: 1.0 μm
Half-ellipsoid tip MWCNT, minor radius 10 nm, major radius 40 nm



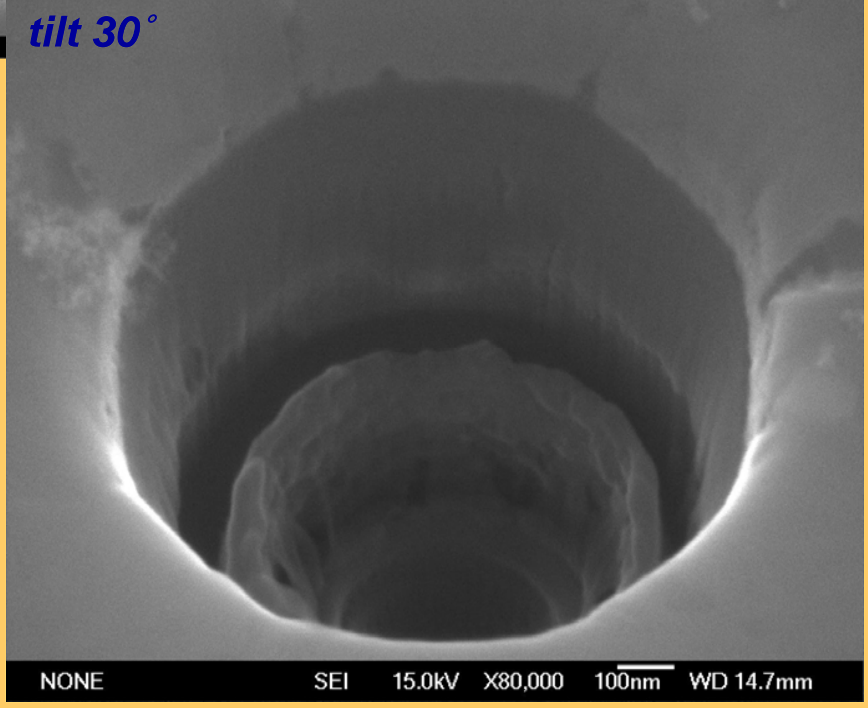
Y. Hu et al. (2004)

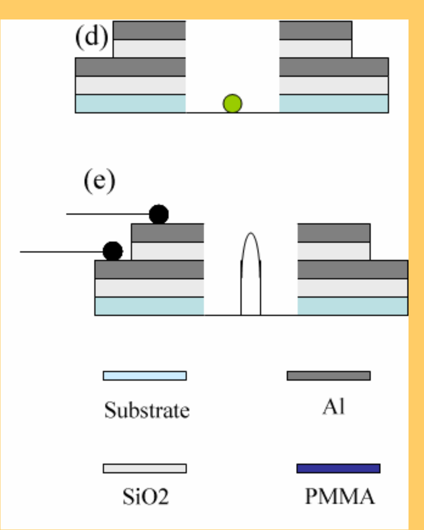
Double gated electrode device





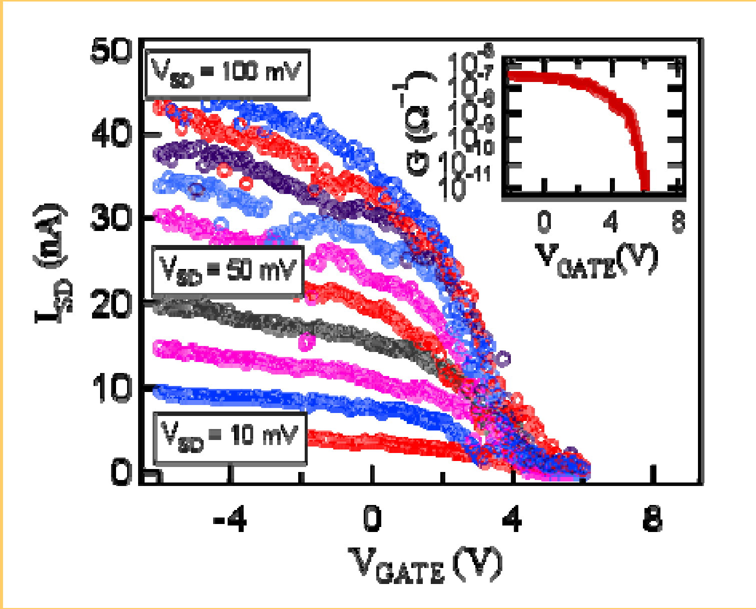
SEM images of double gate electrode device before CNT growth. The aperture size is 1.0 μm.

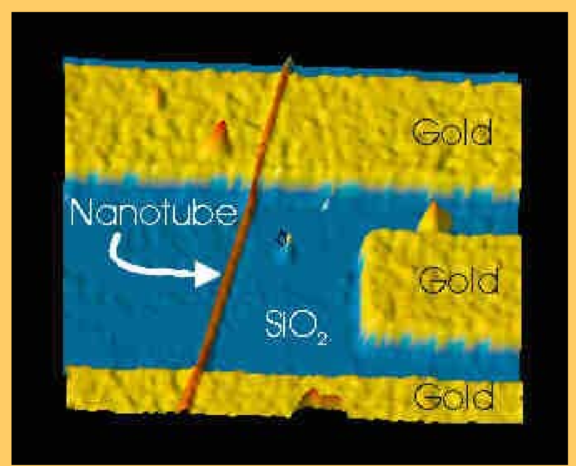


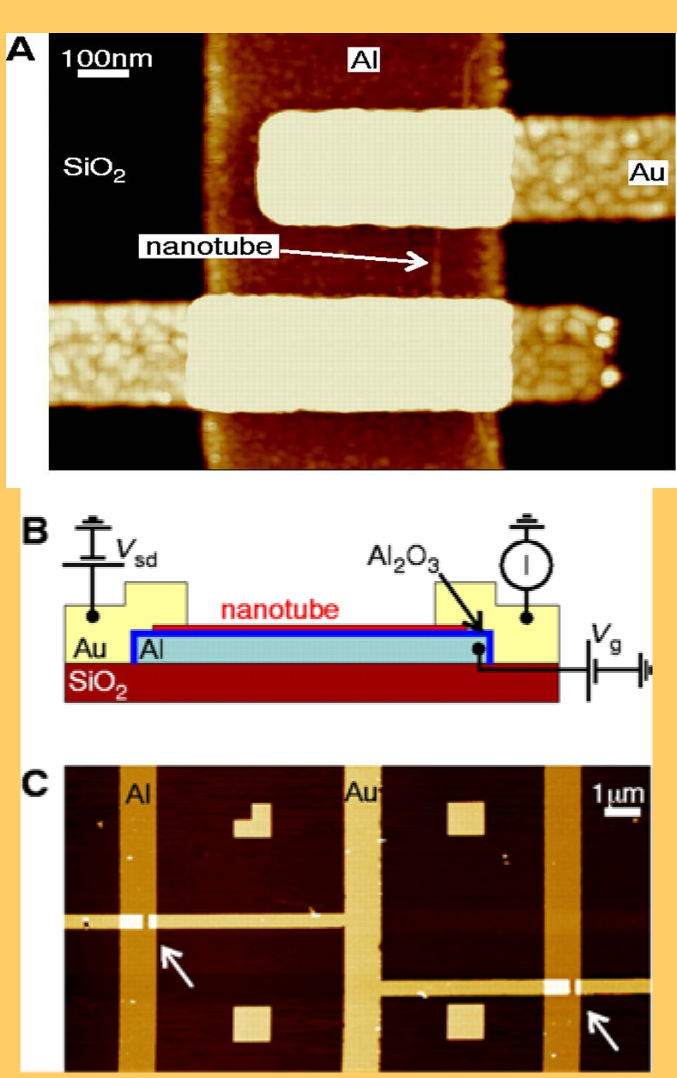


Process for fabricating double gate CNT electrode device : (a) deposition of SiO2 insulator and Al electrode, (b) gate hole fabricated by optical lithography and etching, (c) Resist (PMMA) coating and E-beam lithography, (d) deposition of Ni catalyst followed by lift off, (e) CNT growth by ICP-CVD.

SWNT-based Field Effect Transistor



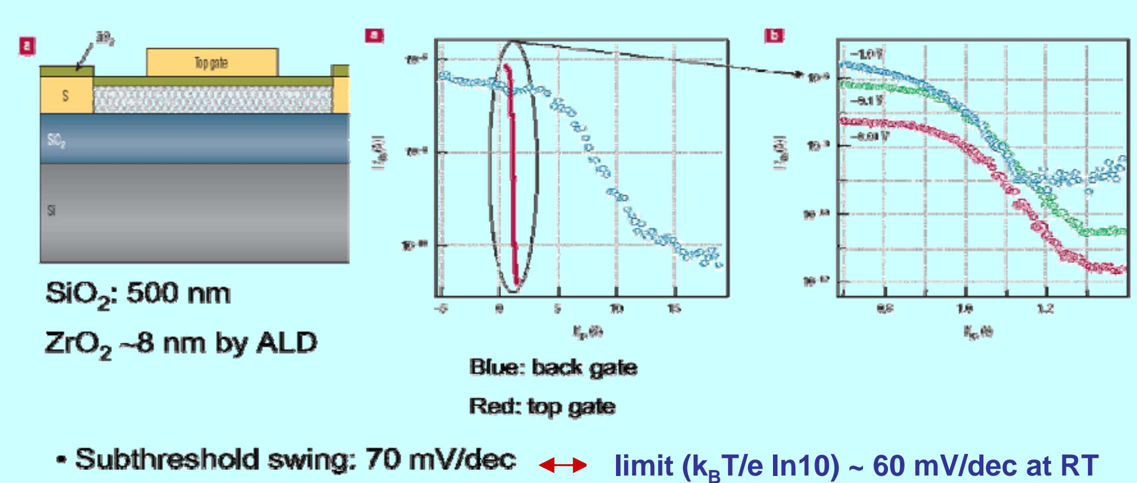


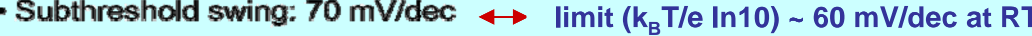


R. Martel, T. Schmidt, H. R. Shea, T. Hertel and Ph. Avouris, *Appl. Phys. Lett.* 73 (1998)

Adrian Bachtold et al, *Science* 294, 2001

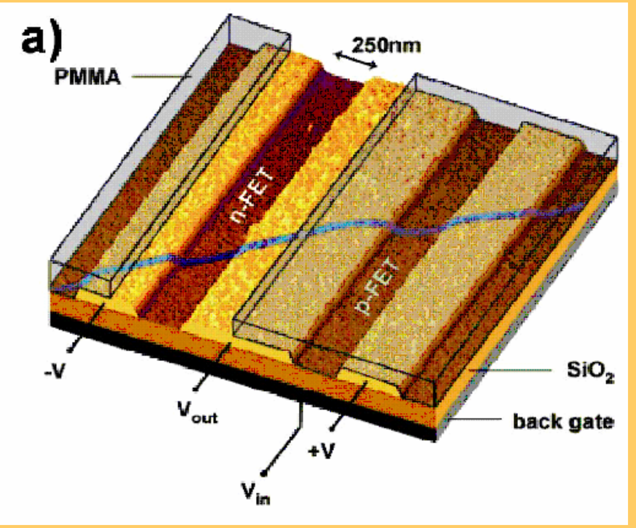
SWNT-based FET and Inverter

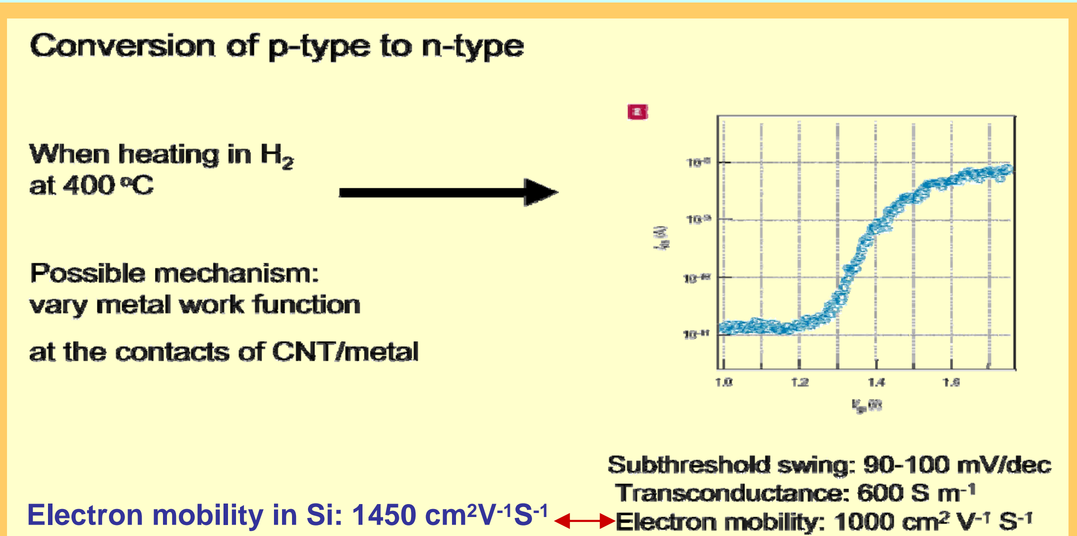




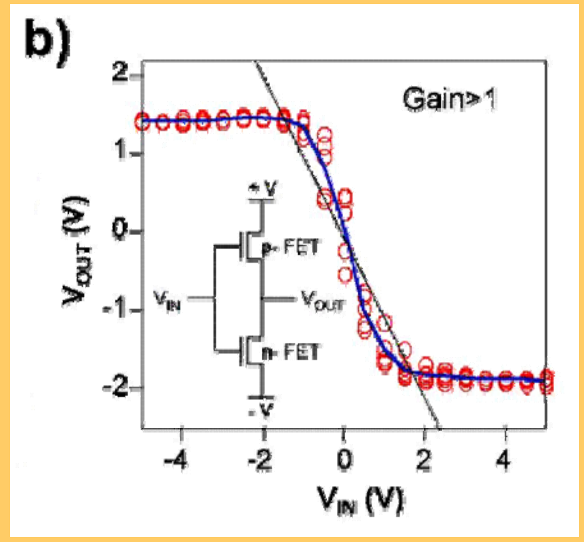
limit (k_BT/e ln10) ~ 60 mV/dec at RT

Hole mobility in Si: 505 $cm^2V^{-1}S^{-1}$





Electron mobility in Si: 1450 $cm^2V^{-1}S^{-1}$



Ali Javey, Hongjie Dai, et al., *Nature* **424**, 654 (2003)

Ph. Avouris, et al., *Nano Letters* **0** (2001)

Challenges for Commercial Applications

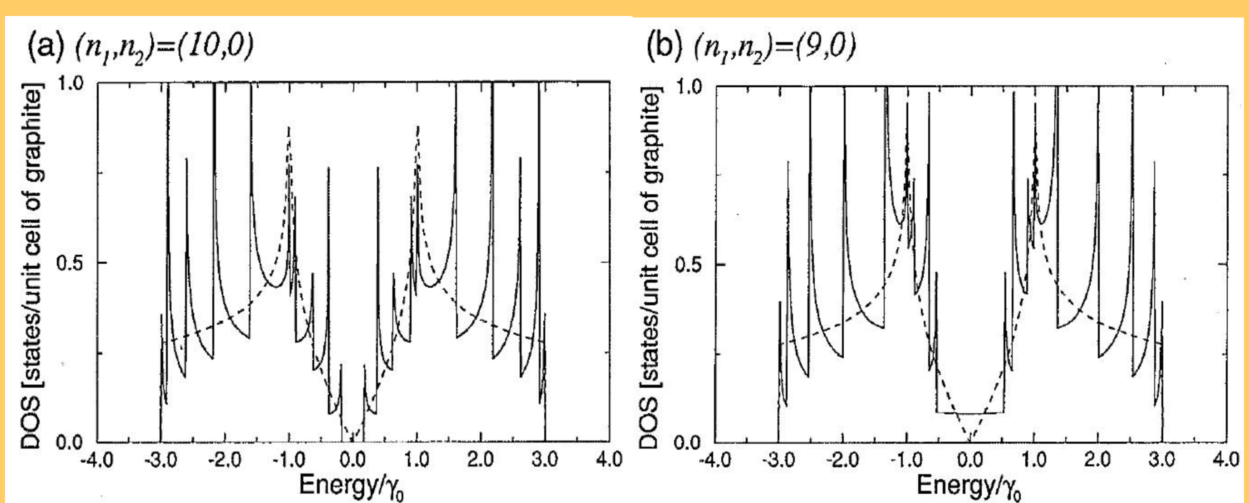
- **Performance Challenges:**

(1) Ambipolar behavior or p-n (n-p) transition due to environment
(2) Strong dependence on the drain voltage
(3) Electron mobility in long channel
(4) Subthreshold slope to thermal limit ~ 60 mV/dec at RT (kT/e ln10)

- SWNT diameter d_l (bandgap ~$1/d_l$)
- Contact metal (Ti, Pd, Al, etc.)
- Gate dielectric thickness & κ

- **Process Challenges:**

(1) Positioning of the SWNTs on the designated locations / direction by *in-situ* catalytic CVD
(2) **Controllability** of desired chirality or **semiconducting** properties of SWNTs
(3) **Low temperature synthesis** techniques for high purity SWNTs
(4) **Low resistance** for SWNTs/metal contacts and controllability on SWNTs/metal Schottky barrier height



R. Saito et al.
***APL* 60 (1992)**

In-situ Growth of SWNTs by Catalytic CVD

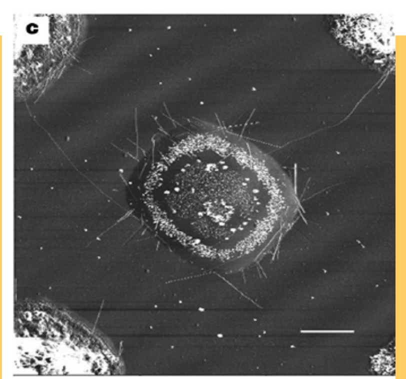
Discrete particles by support materials

* Supported catalyst prepared by impregnation method of metal nitrate followed by baking and mechanical grinding.

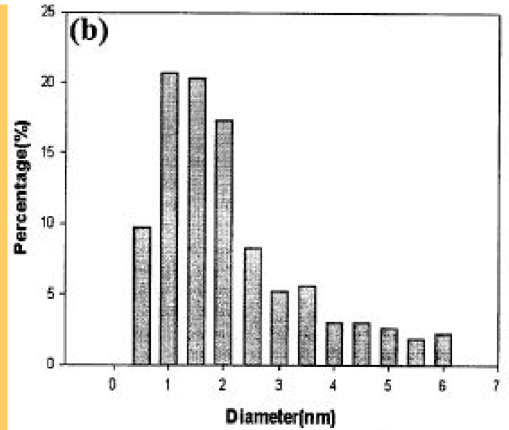
* CVD: methane, 1000℃, min.

Summary of results of methane CVD experiments using supported metal-oxide catalysts

Catalyst composition	Support material	SWNTs?	Description of synthesized material
Fe_2O_3	alumina	yes	abundant individual SWNTs; some bundles; occasional double-walled tubes
Fe_2O_3	silica	yes	abundant SWNT bundles
CoO	alumina	yes	some SWNT bundles and individual SWNTs
CoO	silica	no	no tubular materials synthesized
NiO	alumina	no	mainly defective multi-walled structures with partial metal filling
NiO	silica	no	no tubular materials synthesized
NiO/CoO	alumina	no	no tubular materials synthesized
NiO/CoO	silica	yes	some SWNT bundles



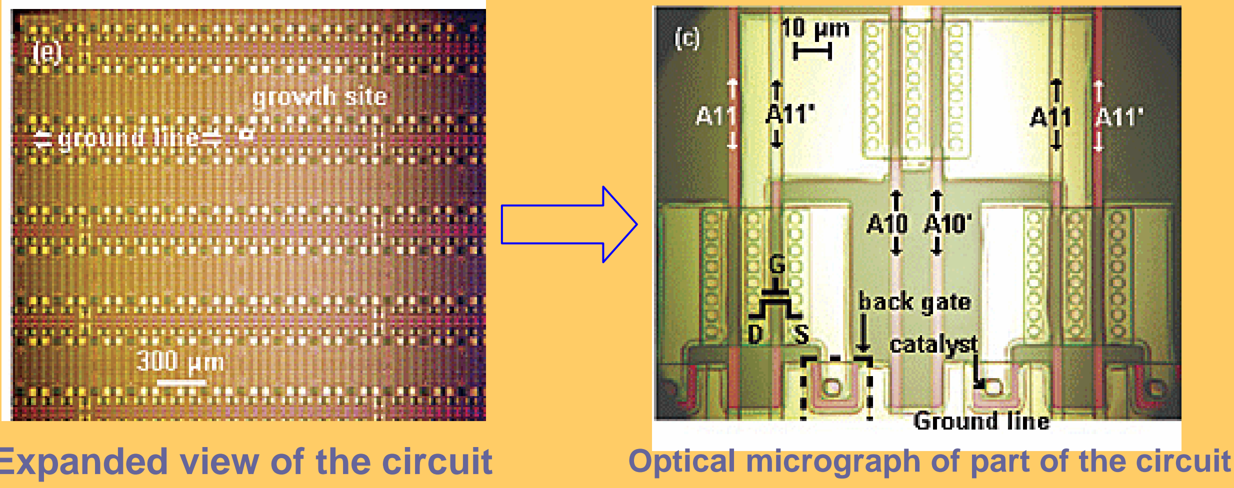
Hongjie Dai et al., *Nature* **395**, 878 - 881 (1998)



➢ **Large diameter dispersion from 0.7 to 6 nm was observed.**

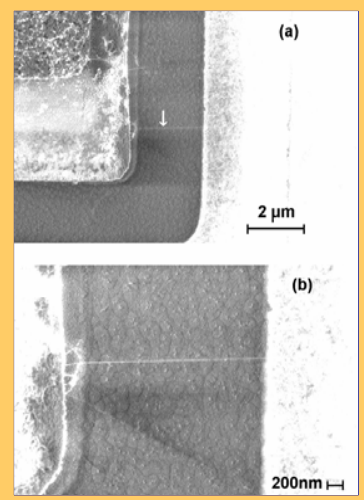
Jing Kong, Alan M. Cassell, Hongjie Dai, *Chem. Phys. Lett.* **292**, 567 (1998)

Carbon Nanotube MOSFETs in The Circuit

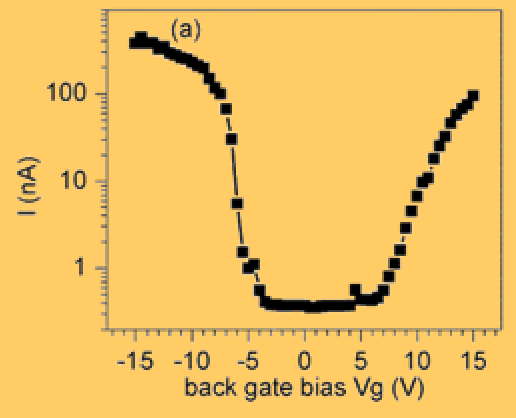


Expanded view of the circuit

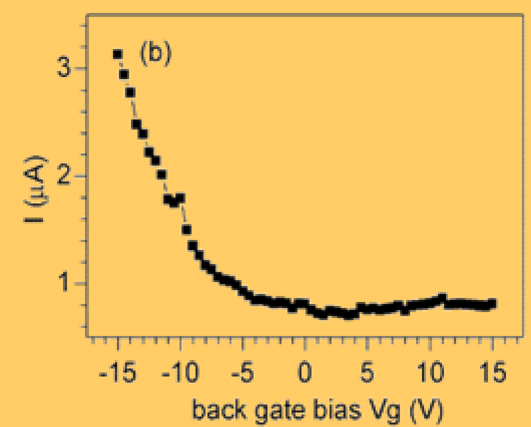
Optical micrograph of part of the circuit



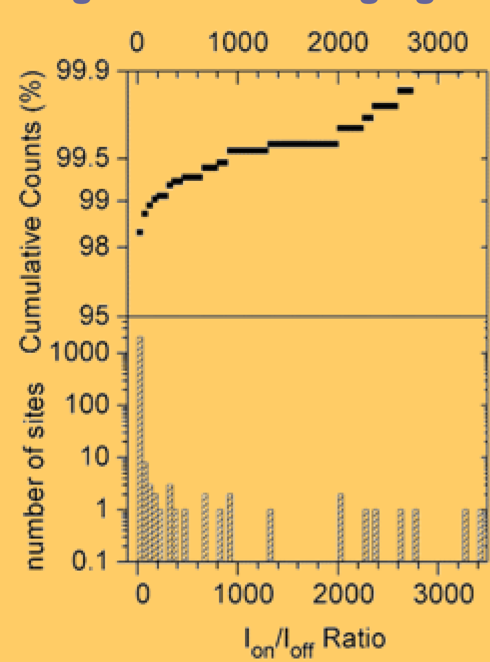
SEM image of a CNT bridging the gap



Ambipolar *I*-*V*g characteristic, at growth site 125.



CNT device exhibiting weak dependence on back gate bias (site 7).



Statistics of electrical measurements on 2048 growth sites.

Yu-Chih Tseng, Hongjie Dai, et al., *Nano Letters* 4 (2004)

SWNTs Growth by Multilayered Metal Catalysts

- Thermal CVD

Mo film ~ 2 Å

Fe film 10 Å

Al film 100 Å

Si substrate

Eight samples:

(a)Fe1/Si

(b)Fe1/SiO_2

(c)Mo0.2/Fe1/Si

(d)Mo0.2/Fe1/SiO_2

(e)Fe1/Al10/Si

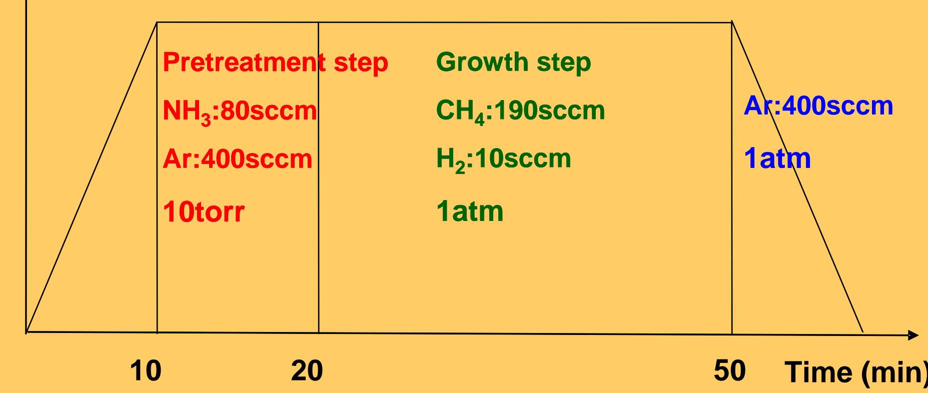
(f)Fe1/Al10/SiO_2

(g)Mo0.2/Fe1/Al10/Si

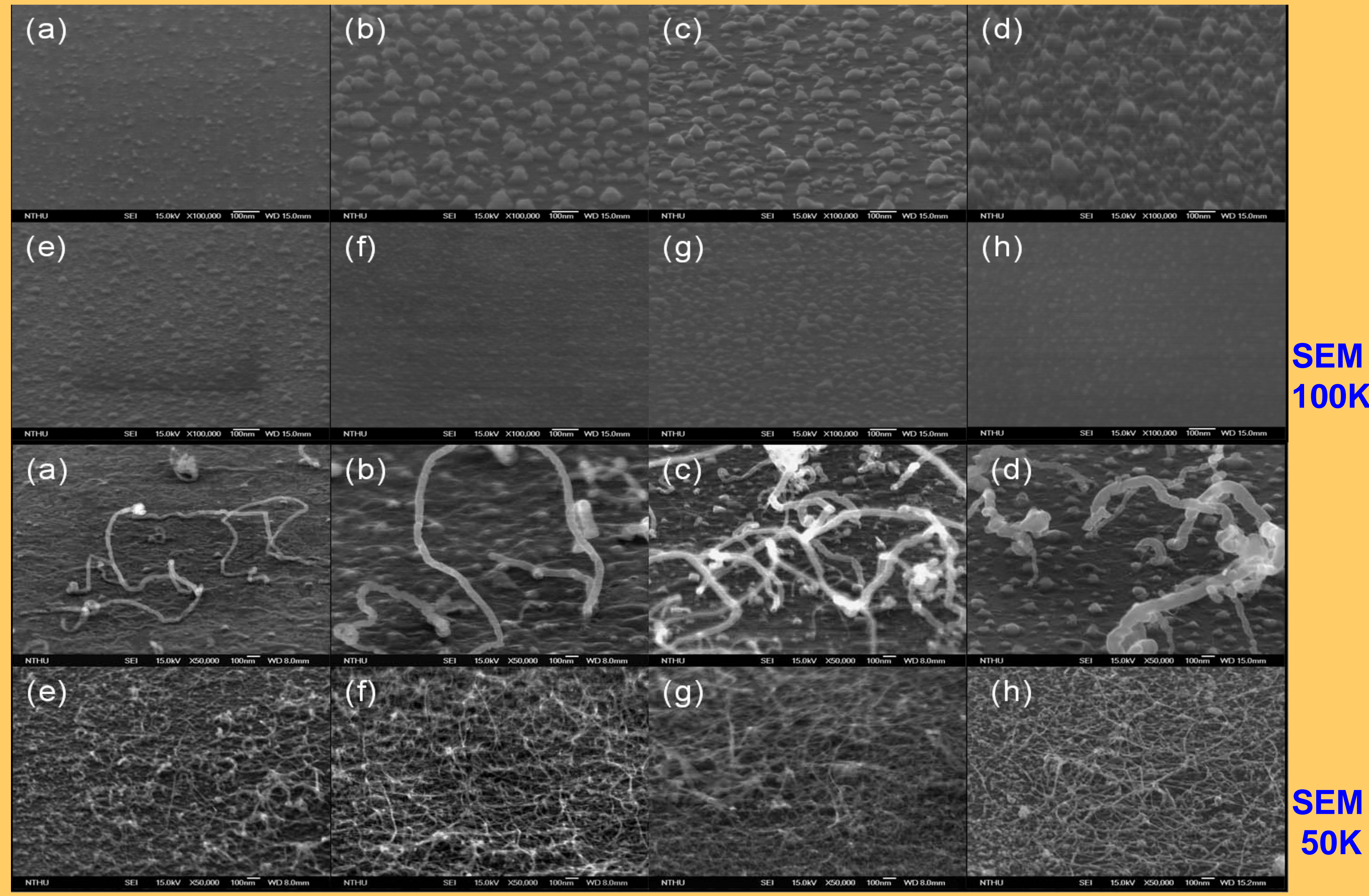
(h)Mo0.2/Fe1/Al10/SiO_2

Process parameter:

900 ℃

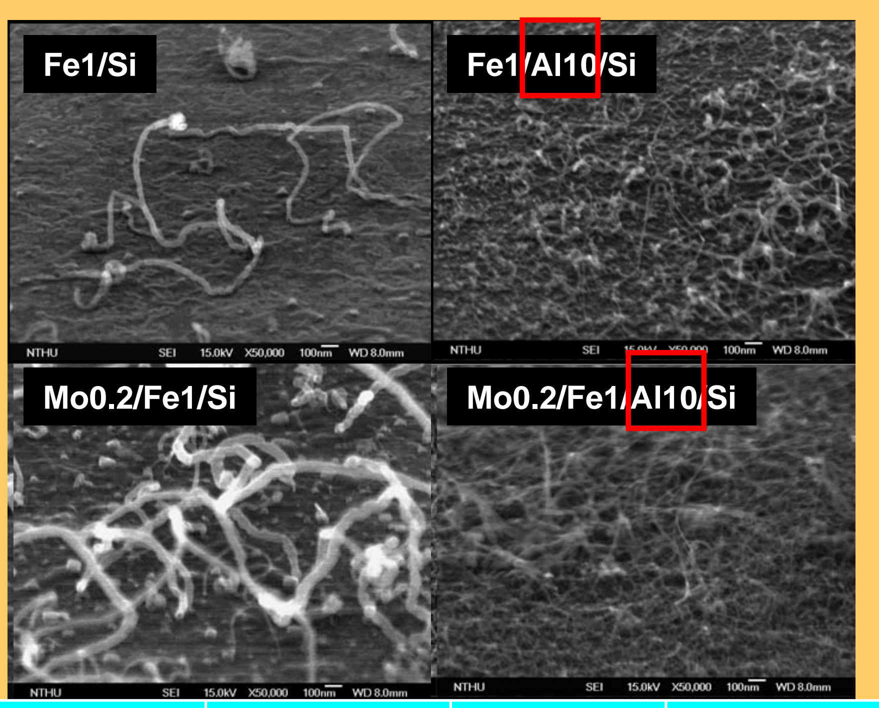


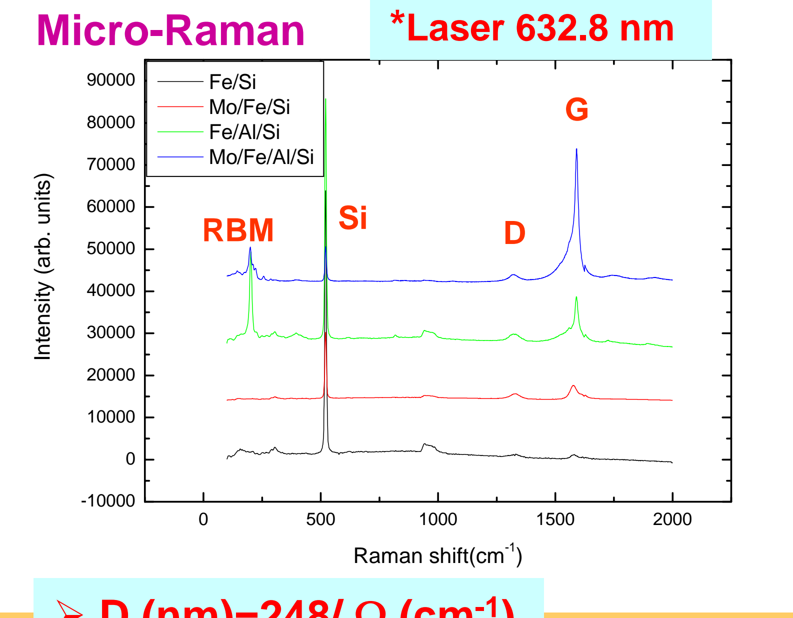
SWNTs Growth by Multilayered Metal Catalysts



(a)Fe1/Si、(b)Fe1/SiO_2、(c)Mo0.2/Fe1/Si、(d)Mo0.2/Fe1/SiO_2、(e)Fe1/Al10/Si、(f)Fe1/Al10/SiO_2、(g)Mo0.2/Fe1/Al10/Si、(h)Mo0.2/Fe1/Al10/SiO_2

SWNTs growth by multilayered metal catalysts



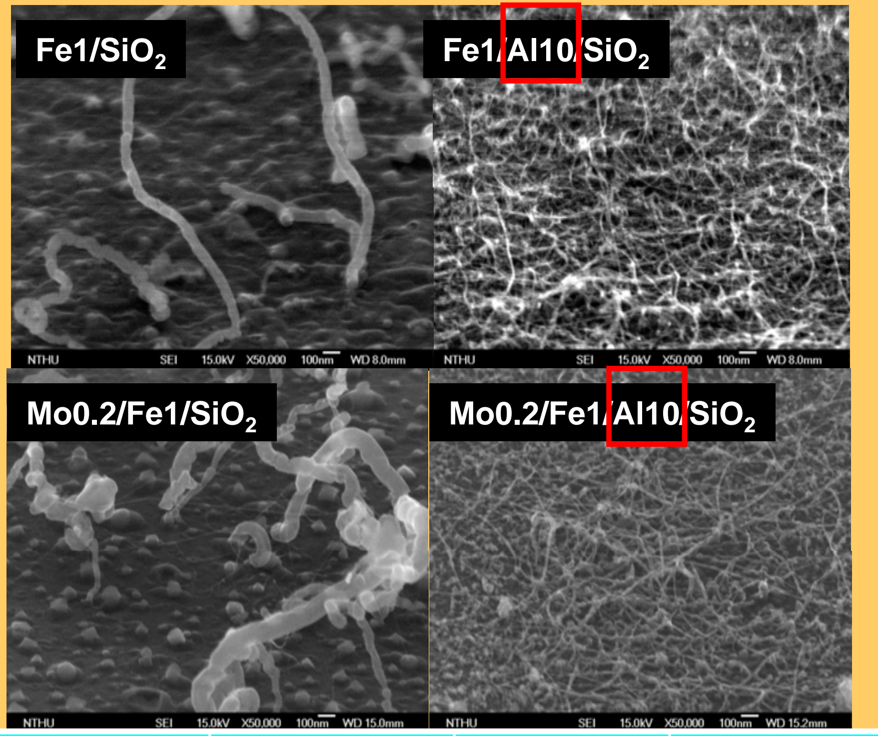


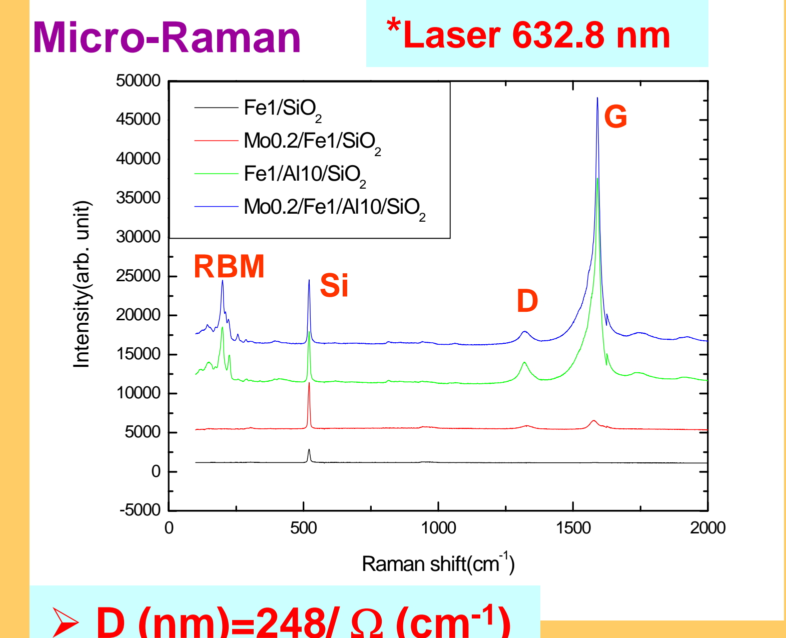
➤ D (nm)=248/ Ω (cm^{-1})

Summary of the process parameters

Method / Sample	Standard Process	Shorter Growth time 5min	Longer Growth time 30min	Lower pressure 100 torr	Lower temperature 800°C	Dilution of hydrocarbon	SWNTs diameter range
Fe1/Si	Rare MWNTs	MWNTs	MWNTs	N/A	None	N/A	None
Mo0.2/Fe1/Si	Rare SWNTs & MWNTs	Mix. SWNTs & MWNTs	Mix. SWNTs & MWNTs	N/A	None	N/A	None
Fe1/Al10/Si	Abundant SWNTs	Rare SWNTs	Abundant SWNTs	Rare SWNTs	None	None	1.265~1.252
Mo0.2/Fe1/Al10/Si	Abundant SWNTs	Abundant SWNTs	Abundant SWNTs	Rare SWNTs	Rare SWNTs	Rare SWNTs	1.258~1.246

SWNTs growth by multilayered metal catalysts





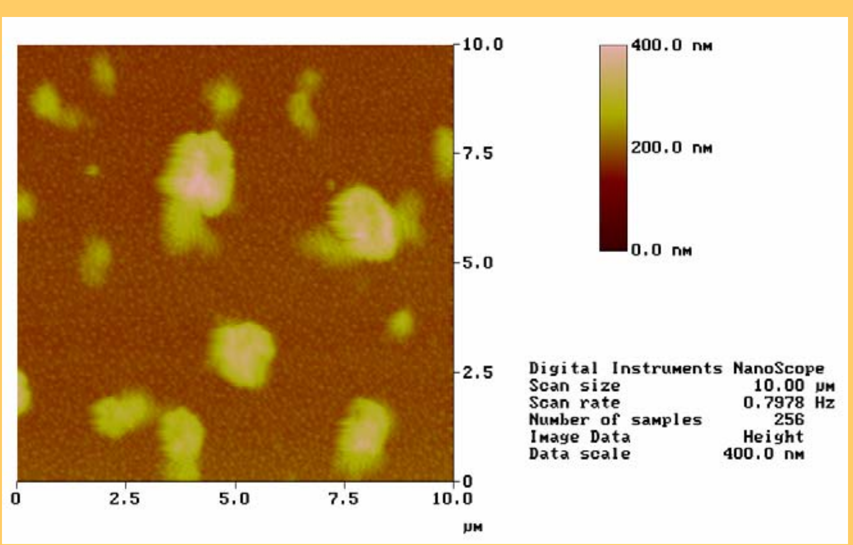
➢ D (nm)=248/ Ω (cm^{-1})

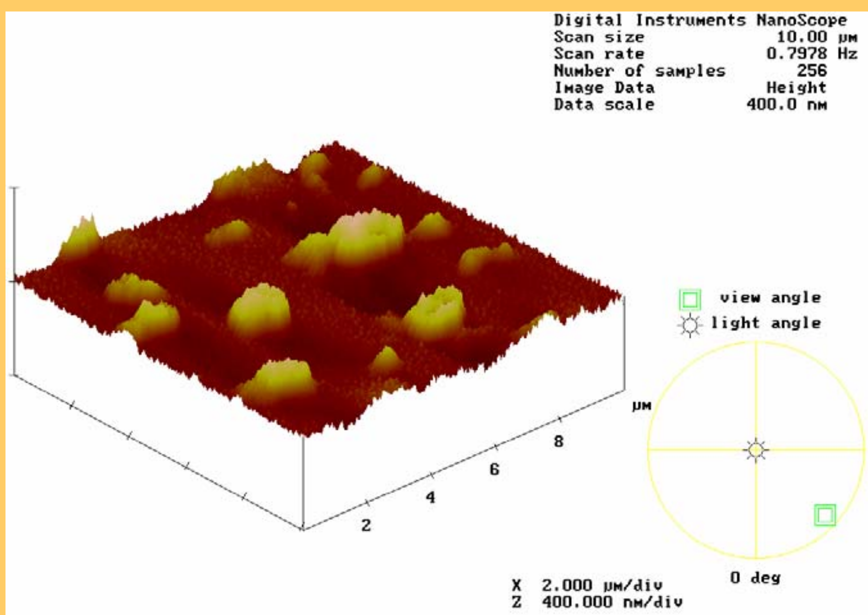
Summary of the process parameters

Method / Sample	Standard Process	Shorter Growth time 5min	Longer Growth time 30min	Lower pressure 100 torr	Lower temperature 800°C	Dilution of hydrocarbon	SWNTs diameter range
$Fe1/SiO_2$	Rare MWNTs	MWNTs	MWNTs	N/A	Rare MWNTs	N/A	None
$Mo0.2/Fe1/SiO_2$	Rare SWNTs & MWNTs	Mix. SWNTs & MWNTs	Mix. SWNTs & MWNTs	N/A	Rare MWNTs	N/A	None
$Fe1/Al10/SiO_2$	Abundant SWNTs	Rare SWNTs	Abundant SWNTs	Rare SWNTs	None	None	1.265~1.252
$Mo0.2/Fe1/Al10/SiO_2$	Abundant SWNTs	Abundant SWNTs	Abundant SWNTs	Rare SWNTs	Rare SWNTs	Rare SWNTs	1.265~1.246

Atomic Force Microscope (AFM) Analysis

Mo0.2/Fe1/Al10/Si





Mo0.2/Fe1/Al10/SiO_2

Clear Execute Undo

Flatten

5.00
2.50
0
2.50
5.00
µm
200.0 nm
100.0 nm
0.0 nm

Digital Instruments NanoScope
Scan size 5.000 µm
Scan rate 0.7978 Hz
Number of samples 256
Image Data Height
Data scale 200.0 nm

Digital Instruments NanoScope
Scan size 5.000 µm
Scan rate 0.7978 Hz
Number of samples 256
Image Data Height
Data scale 200.0 nm

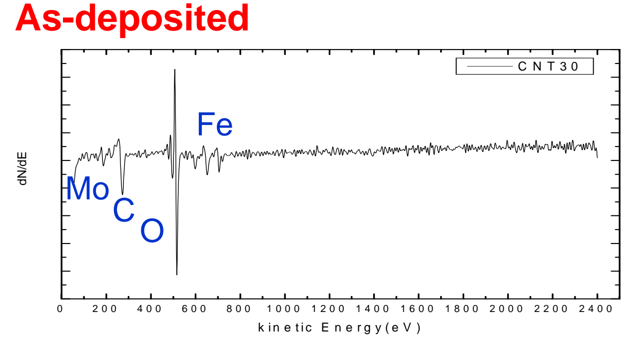
view angle
light angle
µm
1
2
3
4
0 deg
X 1.000 µm/div
Z 200.000 nm/div

fealox_1.002

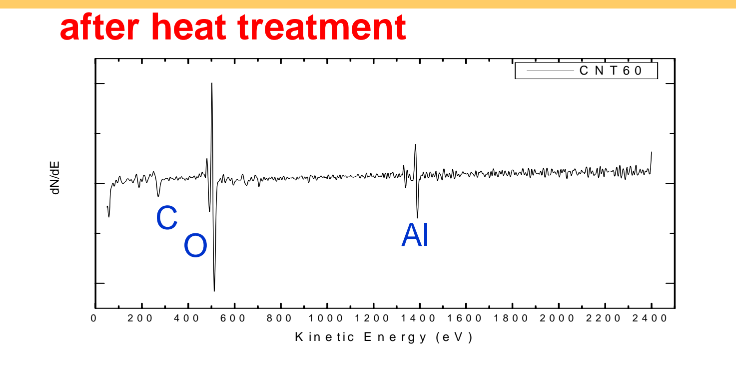
Auger electron spectrometer (AES) analysis

Mo0.2/Fe1/Al10/SiO_2 sample

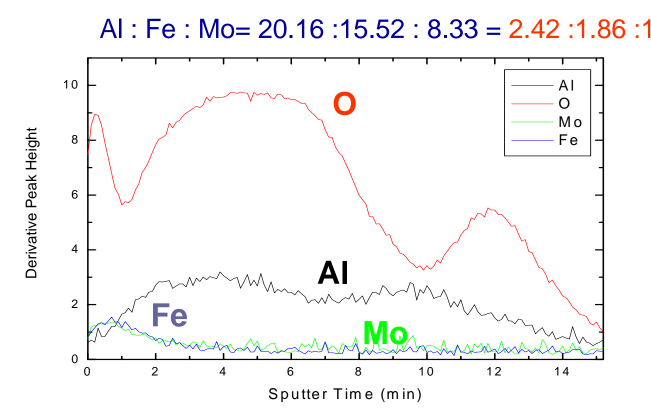
As-deposited

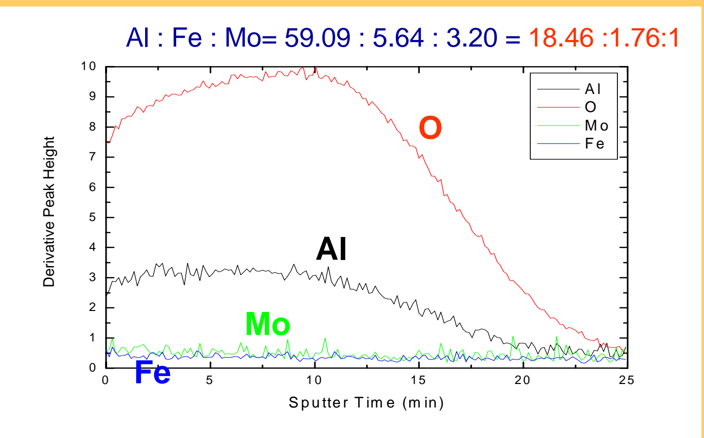


after heat treatment



Depth profile

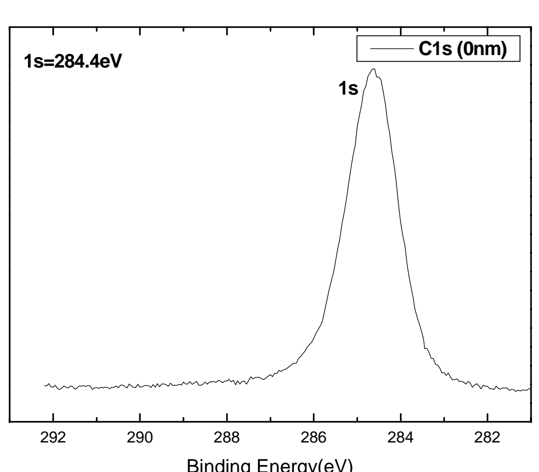




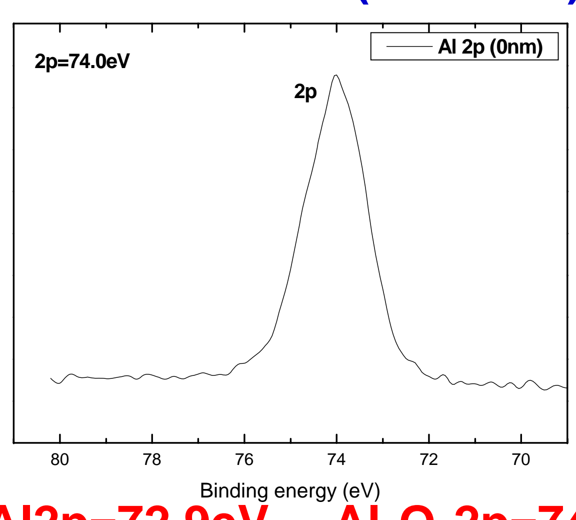
- **Al transformed to aluminum oxide (AlxOy) and retained oxide in the reducing environment which provided a good support material for the catalyst particles.**
- **Fe and Mo were oxidized by the atmosphere before the pretreatment, but the iron oxide and molybdenum oxide were reduced during the pretreatment and retained activity to catalyze the dissociation of hydrocarbon.**

X-Ray Photoelectron Spectroscopy (XPS) Analysis

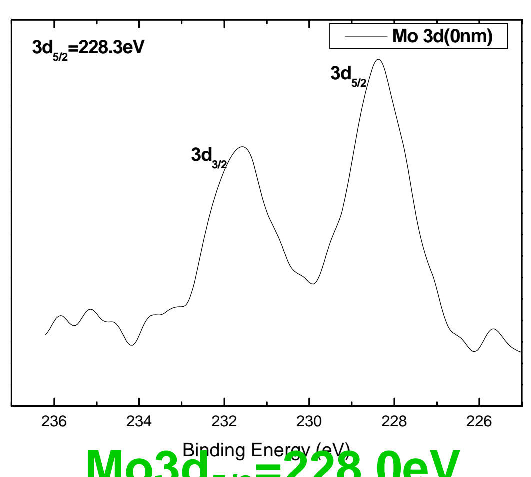
Surface: **after heat treatment**



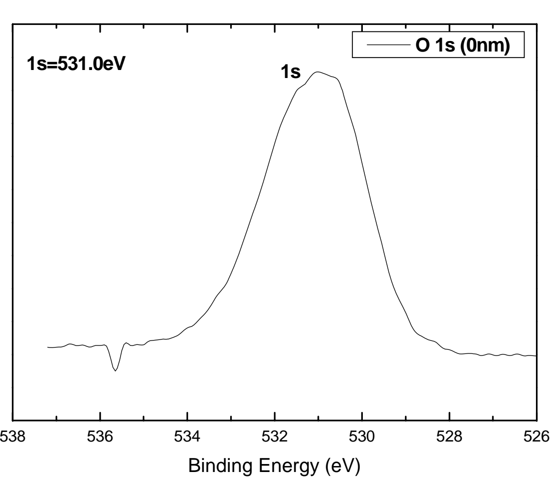
C1s=284.5eV (calibrate)



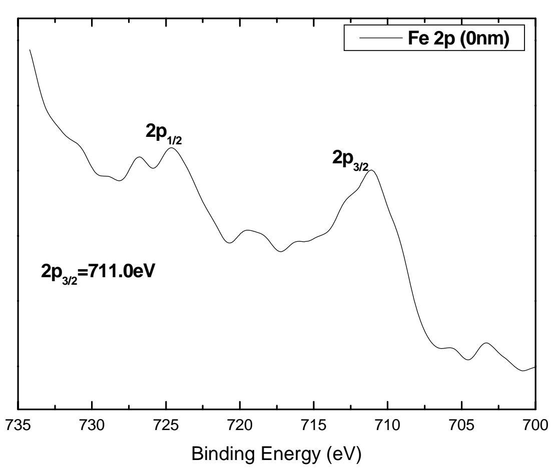
Al2p=72.9eV→ $Al_2O_3$2p=74.4eV



Mo3d$_{5/2}$=228.0eV

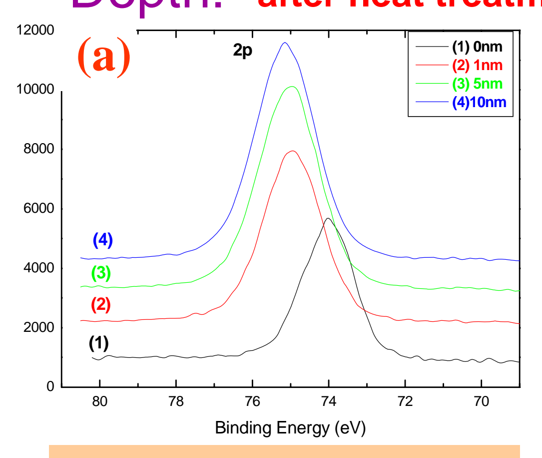


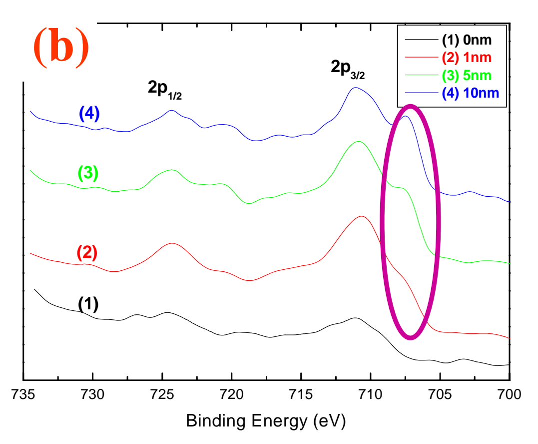
O1s=531.0eV

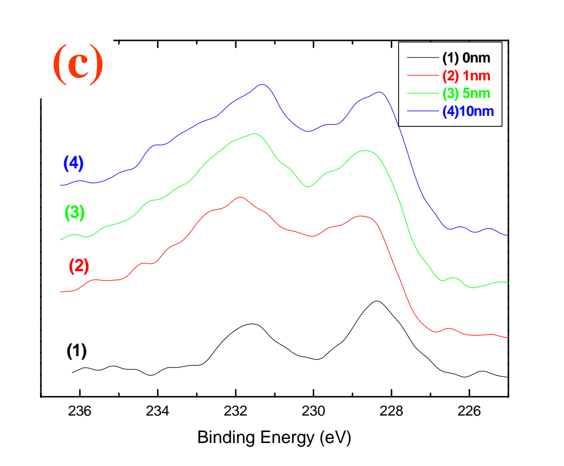


Fe2p$_{3/2}$=707.0eV → $Fe_2O_3$2p$_{3/2}$=710.9eV

X-Ray photoelectron spectroscopy (XPS) analysis







- Al_2O_3,Al2p =74.4eV

(1). 2p = 74.0eV (2). 2p = 74.6 eV (3). 2p = 74.6 eV (4). 2p = 74.9eV

- Fe_2O_3,$Fe2p_{3/2}$=710.9eV → $Fe2p_{3/2}$=707.0eV

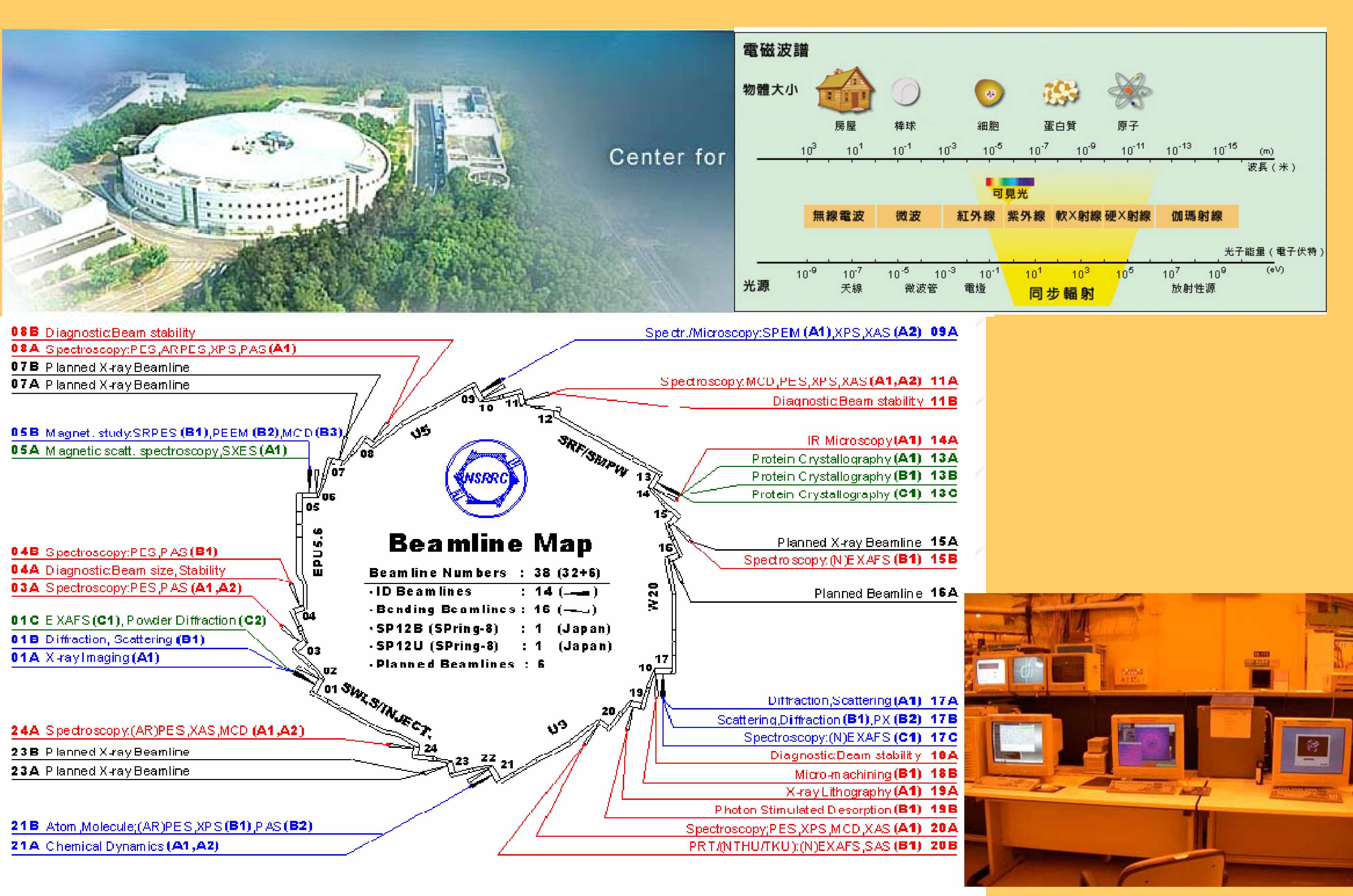
(1). $2p_{3/2}$=711.0eV (2). $2p_{3/2}$=710.9eV (3). $2p_{3/2}$=710.9eV (4). $2p_{3/2}$=710.9eV

- $Mo3d_{5/2}$=228.0eV

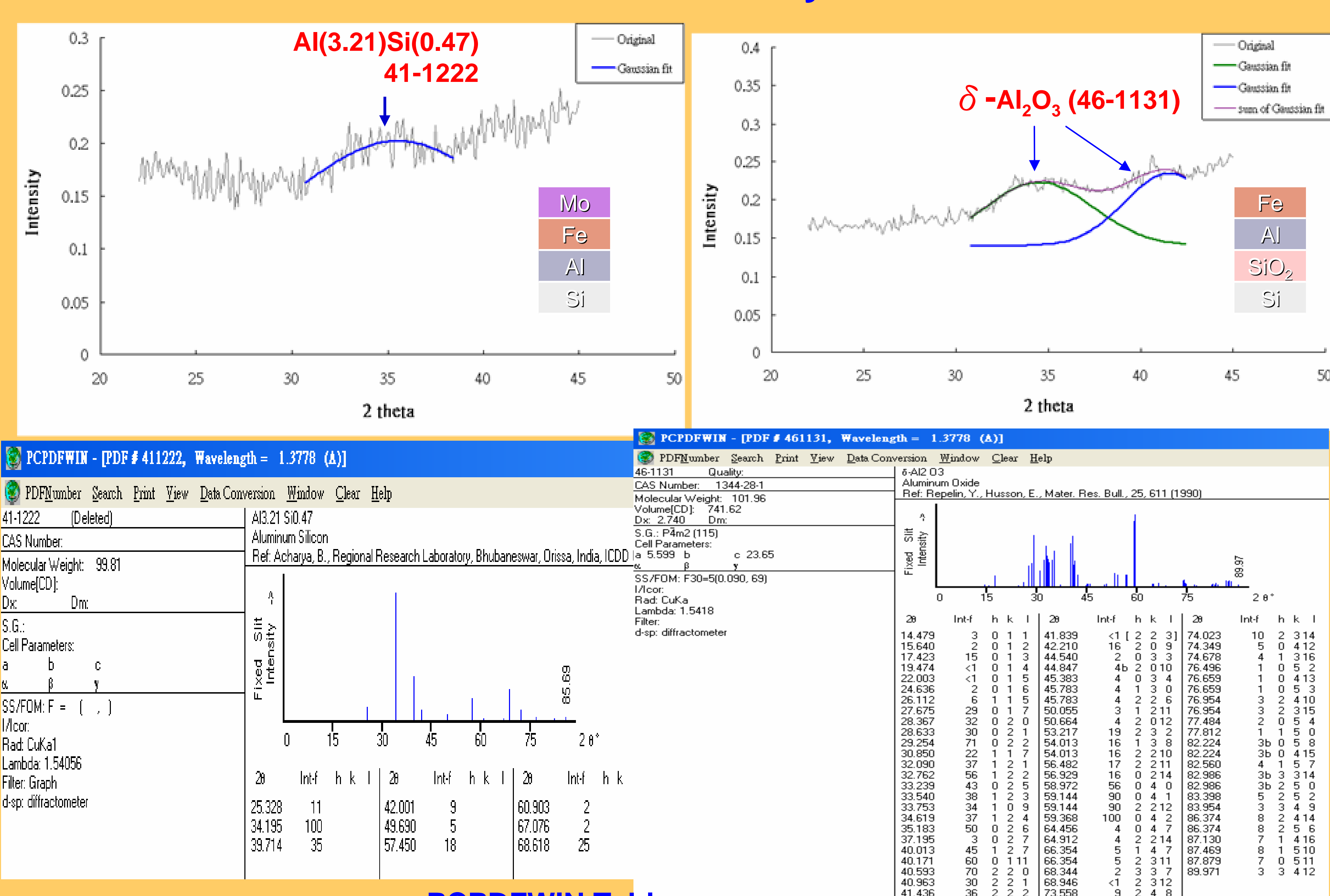
(1). $3d_{5/2}$=228.3eV (2). $3d_{5/2}$=228.6eV (3). $3d_{5/2}$= 228.5eV (4). $3d_{5/2}$= 228.3eV

- To prove the aluminum oxide (AlxOy) is Al_2O_3 and to show the iron oxide and molybdenum oxide were reduced.
- There appeared reduced Fe at ~ 1 nm under surface, therefore the Fe_2O_3 observed on the sample surface after pretreatment was believed due to sample exposure to the atmosphere before the XPS analysis.

NSRRC 17B2 Beam LIine



NSRRC 17B2 Analysis



PCPDFWIN - [PDF # 411222, Wavelength = 1.3778 (A)]

PDFNumber Search Print View Data Conversion Window Clear Help

41-1222 (Deleted)
CAS Number:
Molecular Weight: 99.81
Volume[CD]:
Dx: Dm:
S.G.:
Cell Parameters:
a b c
α β γ
SS/FOM: F = (,)
I/Icor:
Rad: CuKa1
Lambda: 1.54056
Filter: Graph
d-sp: diffractometer

Al3.21 Si0.47
Aluminum Silicon
Ref: Acharya, B., Regional Research Laboratory, Bhubaneswar, Orissa, India, ICDD

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k
25.328	11				42.001	9				60.903	2		
34.195	100				49.690	5				67.076	2		
39.714	35				57.450	18				68.618	25		

PCPDFWIN - [PDF # 461131, Wavelength = 1.3778 (A)]

PDFNumber Search Print View Data Conversion Window Clear Help

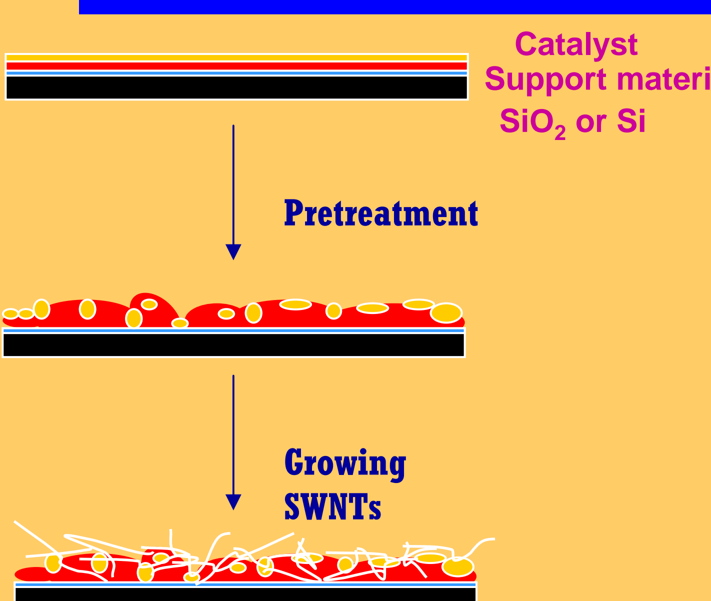
46-1131 Quality:
CAS Number: 1344-28-1
Molecular Weight: 101.96
Volume[CD]: 741.62
Dx: 2.740 Dm:
S.G.: P4m2 (115)
Cell Parameters:
a 5.599 b c 23.65
α β γ
SS/FOM: F30=5(0.090, 69)
I/Icor:
Rad: CuKa
Lambda: 1.5418
Filter:
d-sp: diffractometer

δ-Al2 O3
Aluminum Oxide
Ref: Repelin, Y., Husson, E., Mater. Res. Bull., 25, 611 (1990)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
14.479	3	0	1	1	41.839	<1 [	2	2	3]	74.023	10	2	3	14
15.640	2	0	1	2	42.210	16	2	0	9	74.349	5	0	4	12
17.423	15	0	1	3	44.540	2	0	3	3	74.678	4	1	3	16
19.474	<1	0	1	4	44.847	4b	2	0	10	76.496	1	0	5	2
22.003	<1	0	1	5	45.383	4	0	3	4	76.659	1	0	4	13
24.636	2	0	1	6	45.783	4	1	3	0	76.659	1	0	5	3
26.112	6	1	1	5	45.783	4	2	2	6	76.954	3	2	4	10
27.675	29	0	1	7	50.055	3	1	2	11	76.954	3	2	3	15
28.367	32	0	2	0	50.664	4	2	0	12	77.484	2	0	5	4
28.633	30	0	2	1	53.217	19	2	3	2	77.812	1	1	5	0
29.254	71	0	2	2	54.013	16	1	3	8	82.224	3b	0	5	8
30.850	22	1	1	7	54.013	16	2	2	10	82.224	3b	0	4	15
32.090	37	1	2	1	56.482	17	2	2	11	82.560	4	1	5	7
32.762	56	1	2	2	56.929	16	0	2	14	82.986	3b	3	3	14
33.239	43	0	2	5	58.972	56	0	4	0	82.986	3b	2	5	0
33.540	38	1	2	3	59.144	90	0	4	1	83.398	5	2	5	2
33.753	34	1	0	9	59.144	90	2	2	12	83.954	3	3	4	9
34.619	37	1	2	4	59.368	100	0	4	2	86.374	8	2	4	14
35.183	50	0	2	6	64.456	4	0	4	7	86.374	8	2	5	6
37.195	3	0	2	7	64.912	4	2	2	14	87.130	7	1	4	16
40.013	45	1	2	7	66.354	5	1	4	7	87.469	8	1	5	10
40.171	60	0	1	11	66.354	5	2	3	11	87.879	7	0	5	11
40.593	70	2	2	0	68.344	2	3	3	7	89.971	3	3	4	12
40.963	30	2	2	1	68.946	<1	2	3	12					
41.436	36	2	2	2	73.558	9	2	4	8					

PCPDFWIN Table

The Growth Model of SWNTs



1. Multilayered catalysts were oxidized by the atmosphere.
2. Al_2O_3 was retained oxide and the Fe_2O_3 was reduced to Iron by the pretreatment.
3. Al_2O_3 acted the role of support material and prevented the catalyst particles to aggregate.
4. SWNTs grown on small catalyst particles.

Function of Al :

Aluminum oxide acts as a good support material for the catalyst

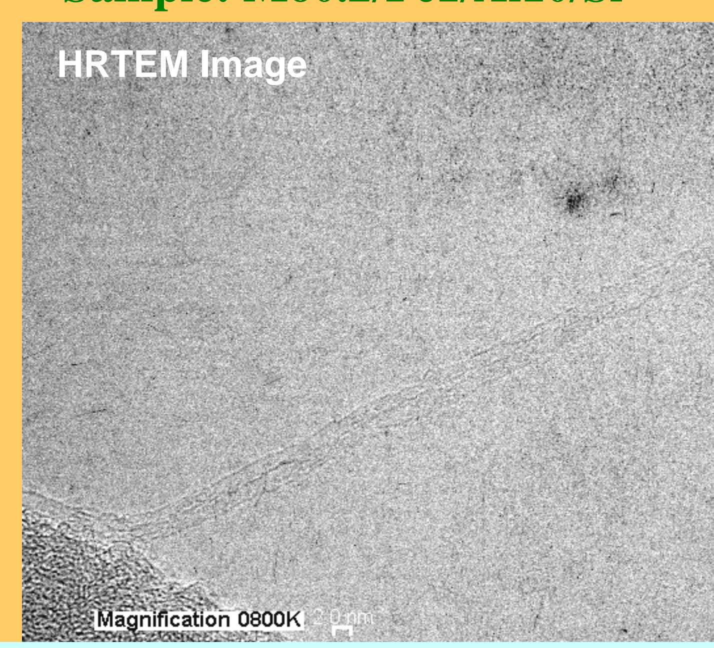
- the catalysts are hindered to aggregate to form large particles.
- provide more active nucleation sites.
- provide a porous underlayer, allowing for methane gas to flow to Fe surface.

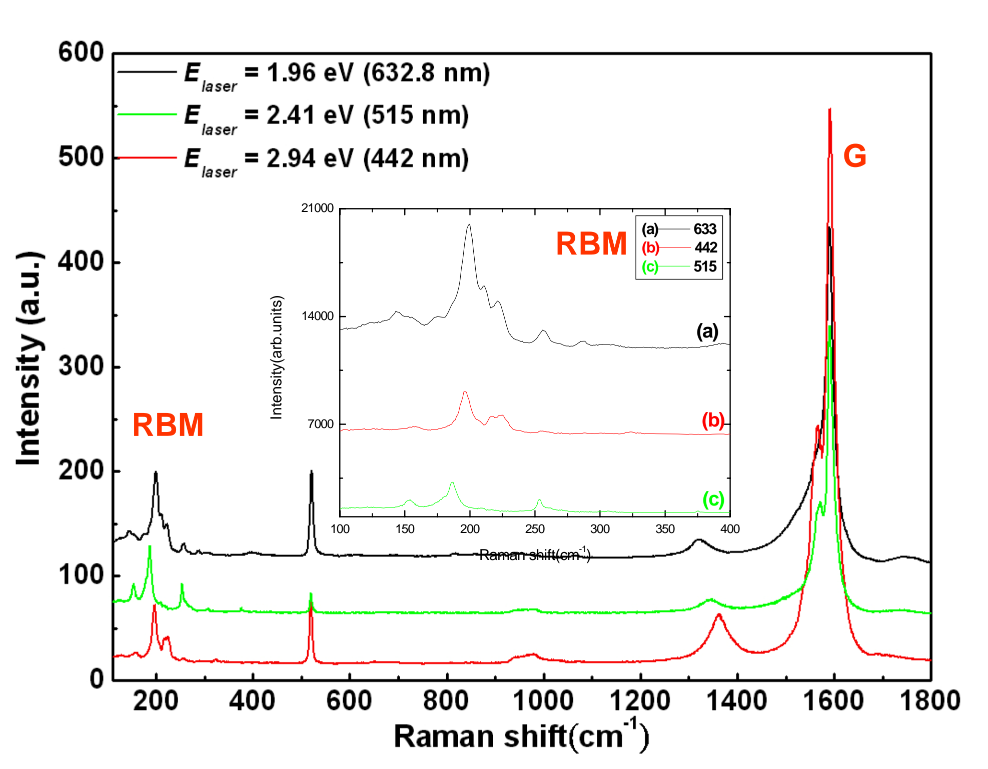
Function of Mo:

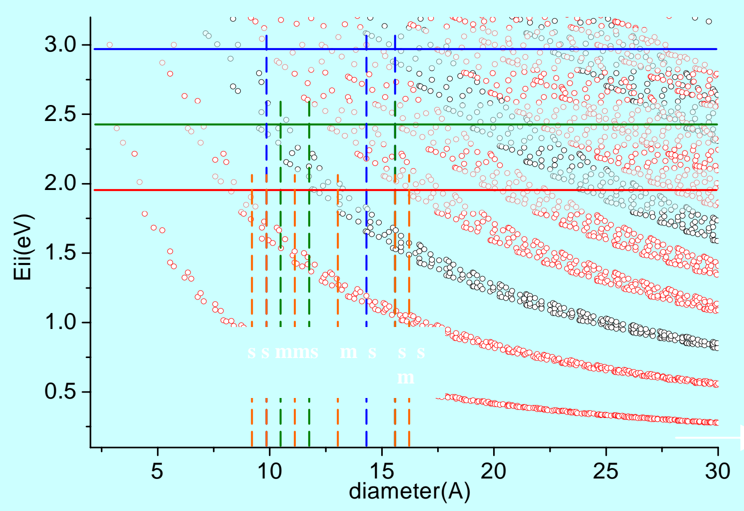
- Mo may help to promote the reduction of iron and retain catalytically active during the growth process.
- Mo is known to be a catalyst center for promoting the aromatization of methane, providing the intermediate aromatic species which can feed into the adjacent Fe sites with high efficiency.
- In the methane environment, Mo may exist in the form of Mo2C and MoO3 which may probably inhibit the aggregation of iron particles. (but not observed in this study)

Different Laser Wavelengths for Raman Analysis

Sample: Mo0.2/Fe1/Al10/Si



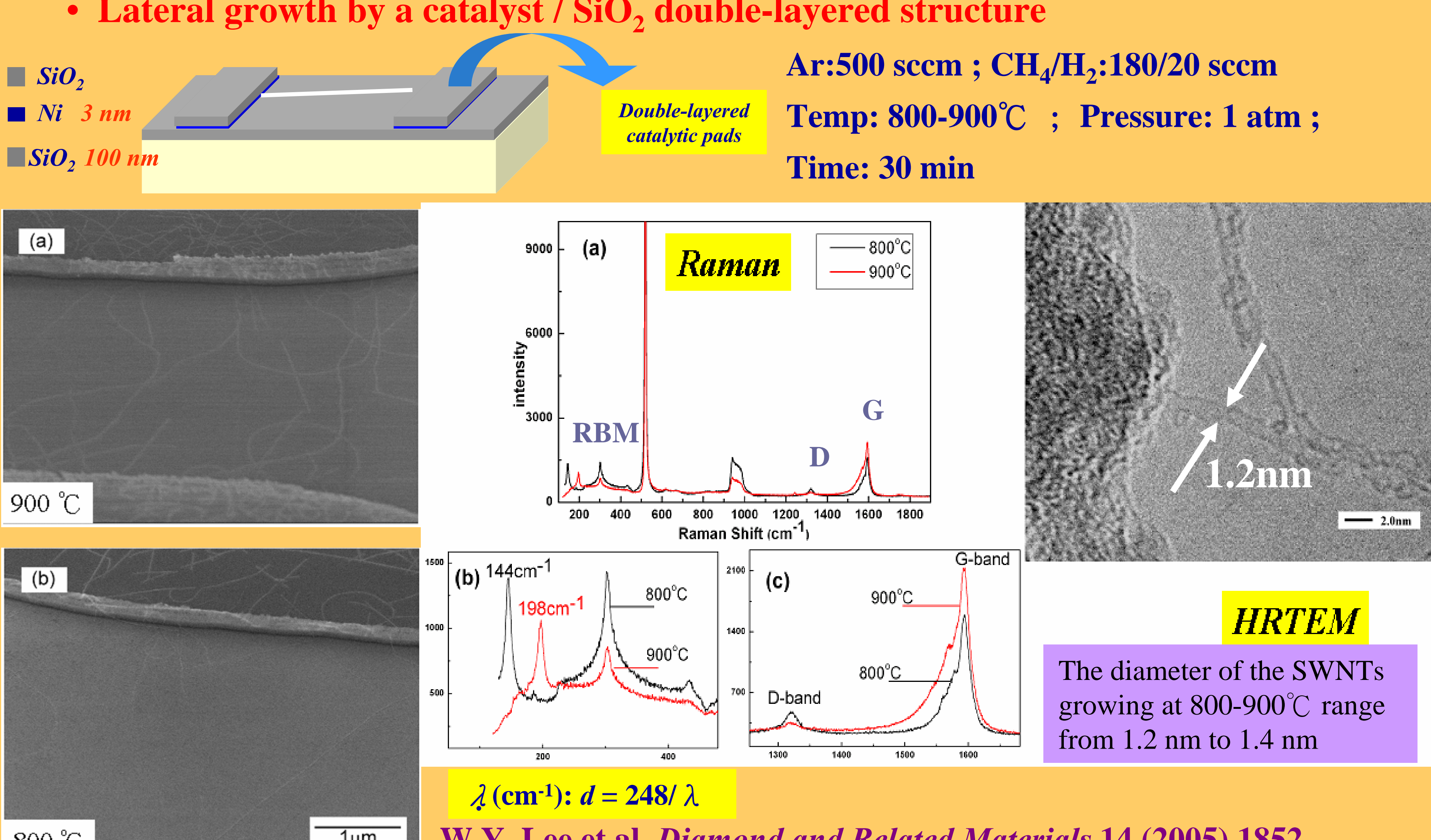




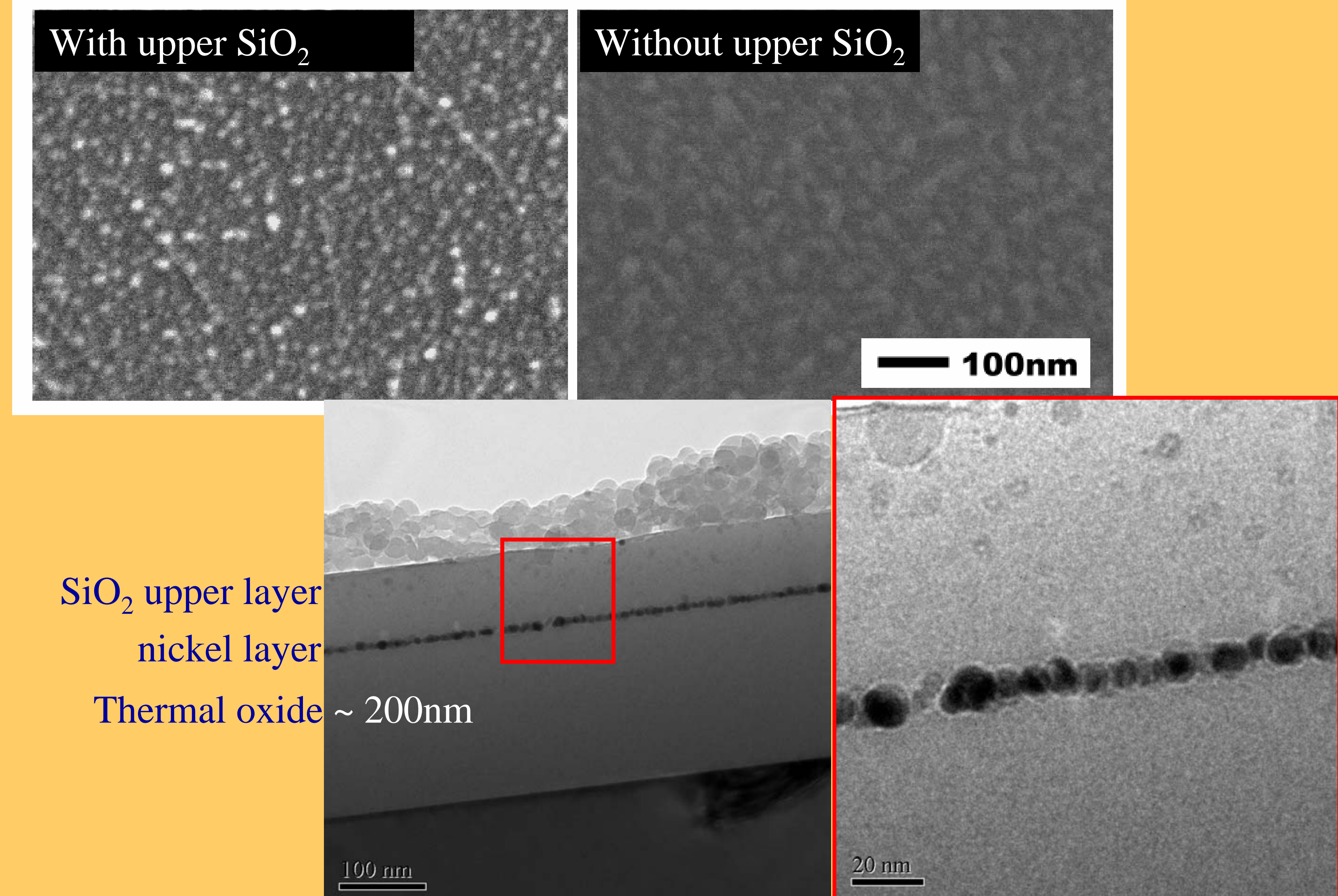
- There appeared RBM peaks in all different laser wavelengths in Raman analyses, and all have high *ID/IG* ratio.
- The only difference is the RBM position, and the resonance position is 199 cm^{-1}, 196 cm^{-1}, 187 cm^{-1} in the wavelength 633 nm, 442 nm, 515 nm respectively.

existing metallic and semiconducting tubes

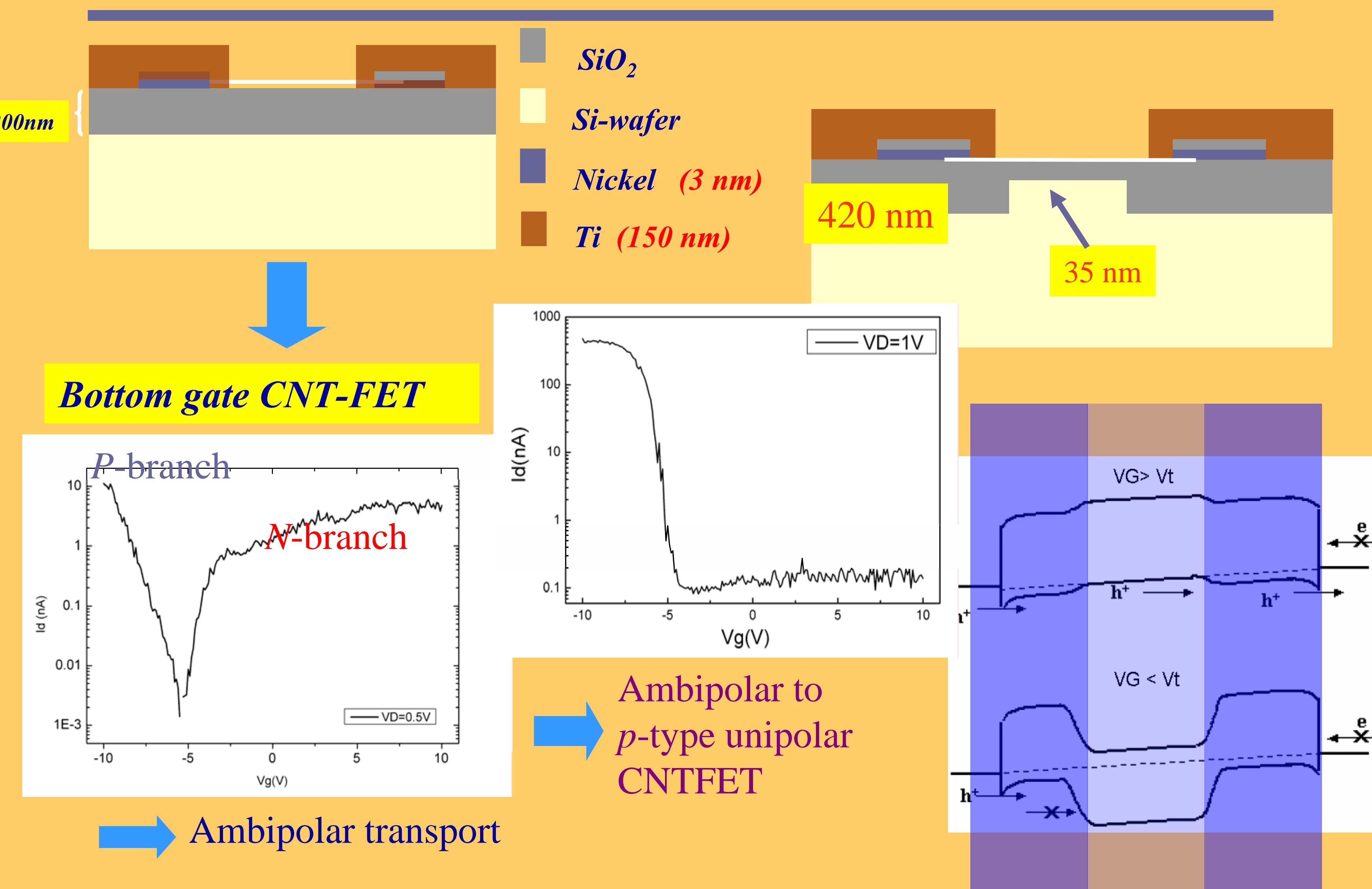
Controlled *in-situ* Growth of Single-walled Carbon Nanotubes for Field-Effect-Transistor Application



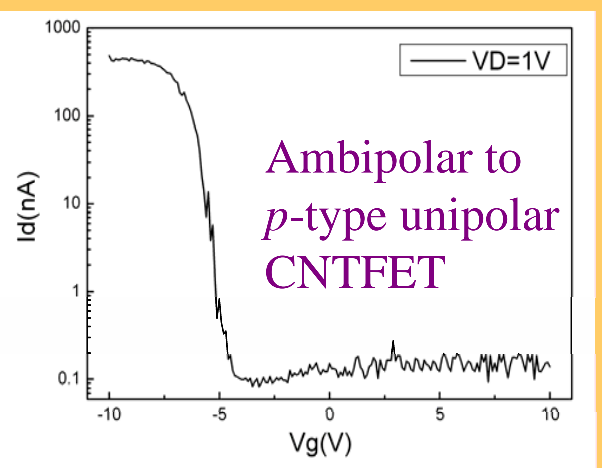
Cross-section TEM of double layer

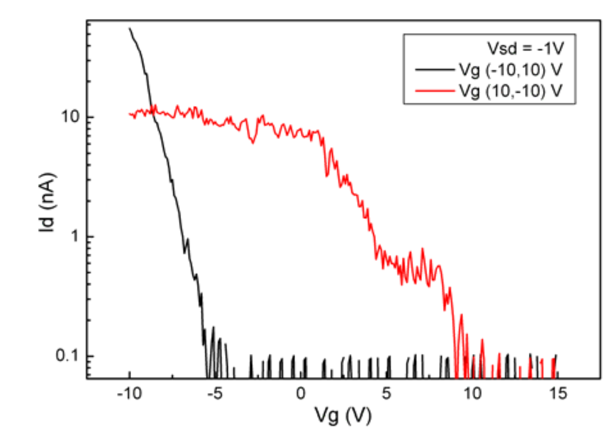


Field Effect free-on source/drain electrodes



Asymmetric Structure CNTFET

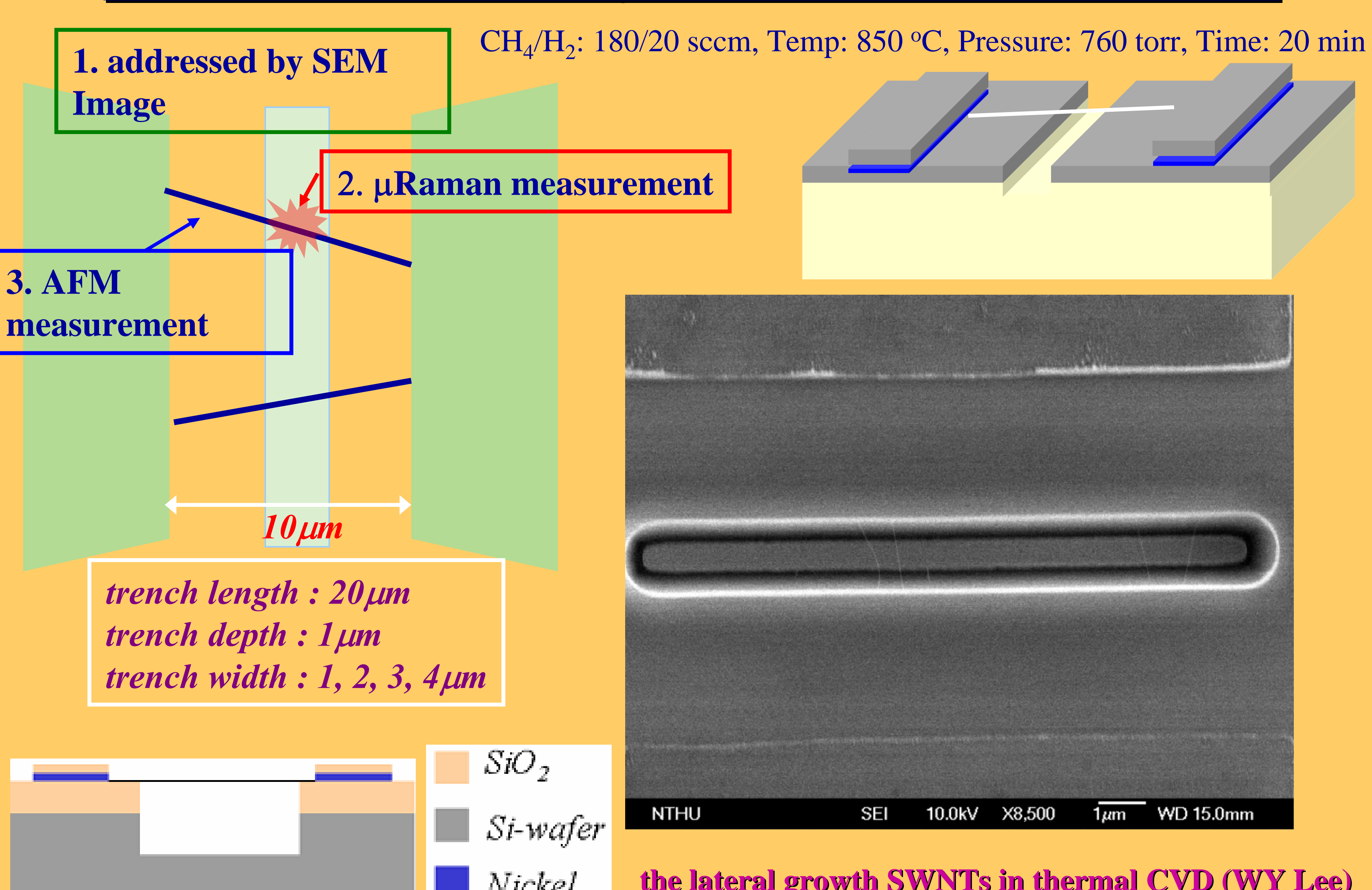




P-type and hysteresis behavior in air

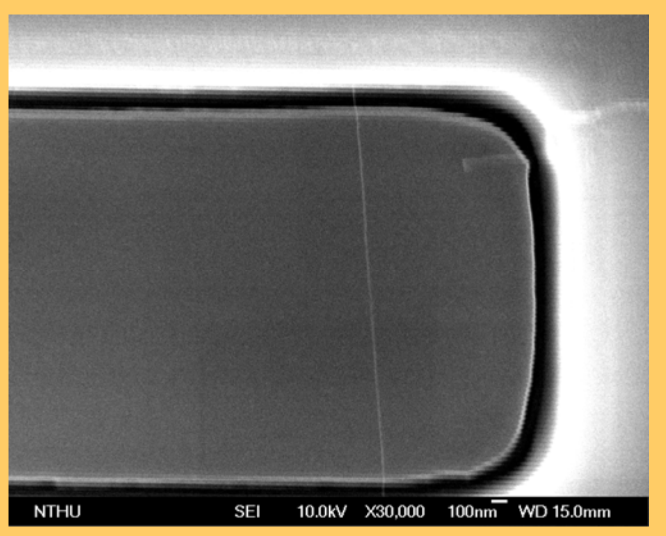
	Thin-oxide CNT-FET	CNT-FET with field -effect-free-on source/drain structure	Asymmetric CNT-FET
Threshold Voltage (V)	-7.1	-5.7	-9.8
Subthreshold Swing (mV/dec)	1170	543.1	429
I_{on} (nA)	11.1	476.4	149
I_{off} (nA)	0.0014	0.09458	0.02
On/Off Ratio	7929	5037	7450
Behavior	Ambipolar	Unibipolar	Unibipolar

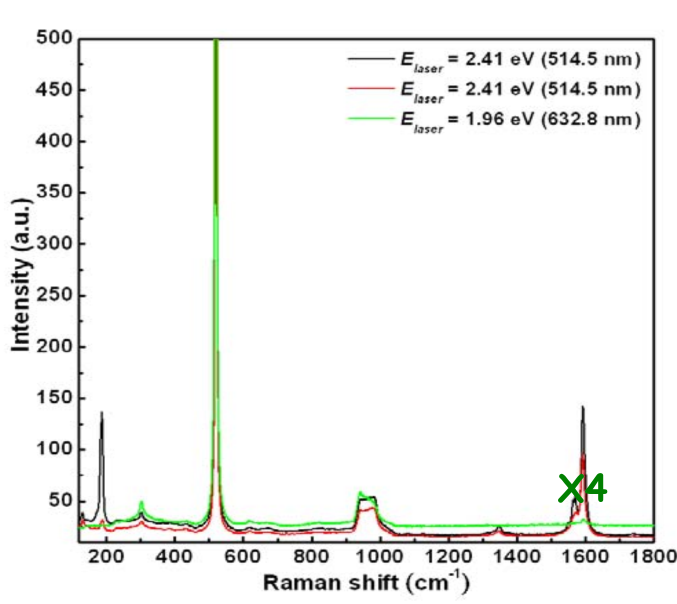
Charaterization by suspended structure



the lateral growth SWNTs in thermal CVD (WY Lee)

Raman spectrum of an assemble su-SWNTs





Raman shift (cm^{-1})

E_{ii} (eV)

SWNT diameter (nm)

We can see the different resonant window !

assignment

Intensity (a.u.)

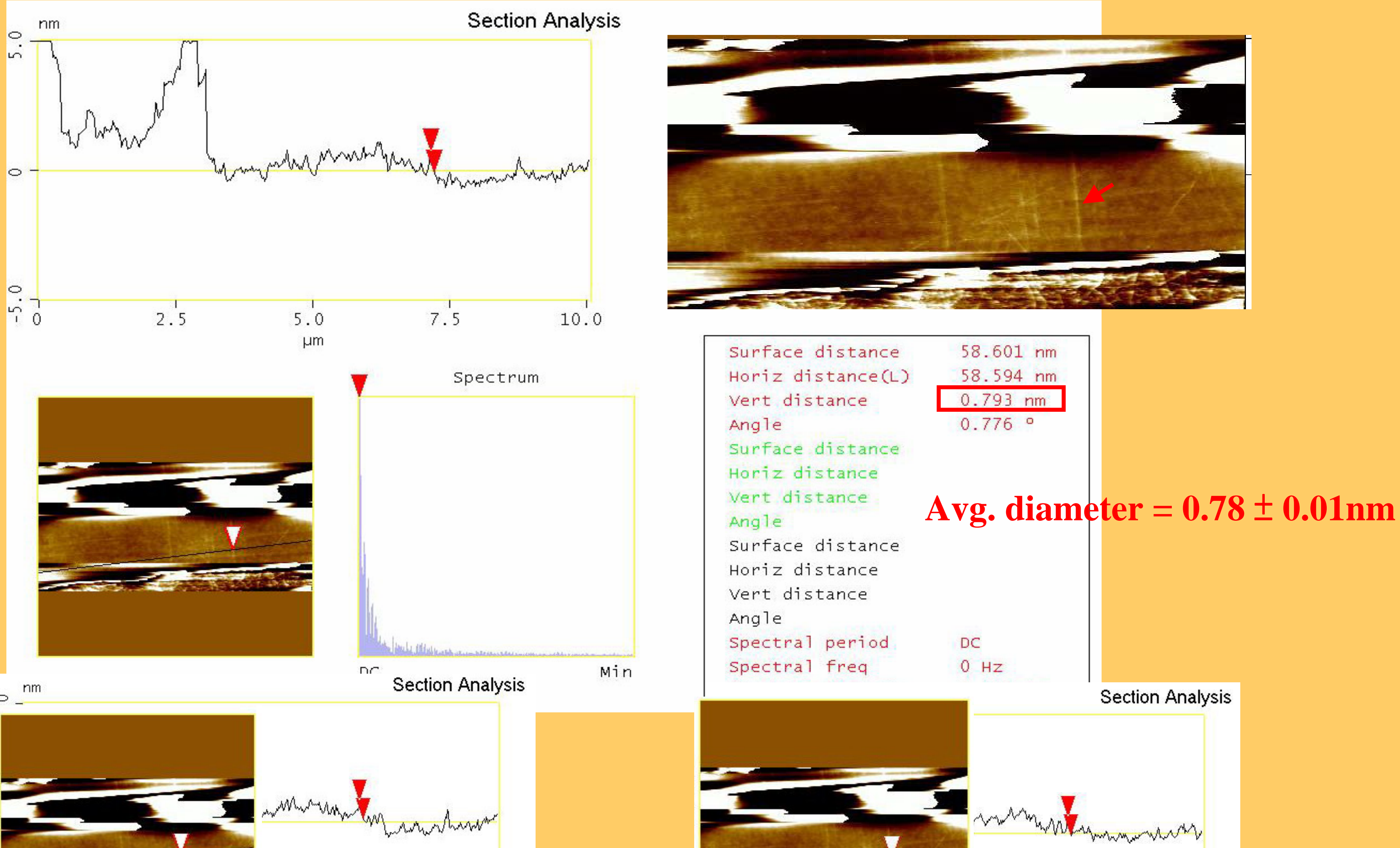
resonance

no resonance

Raman shift (cm^{-1})

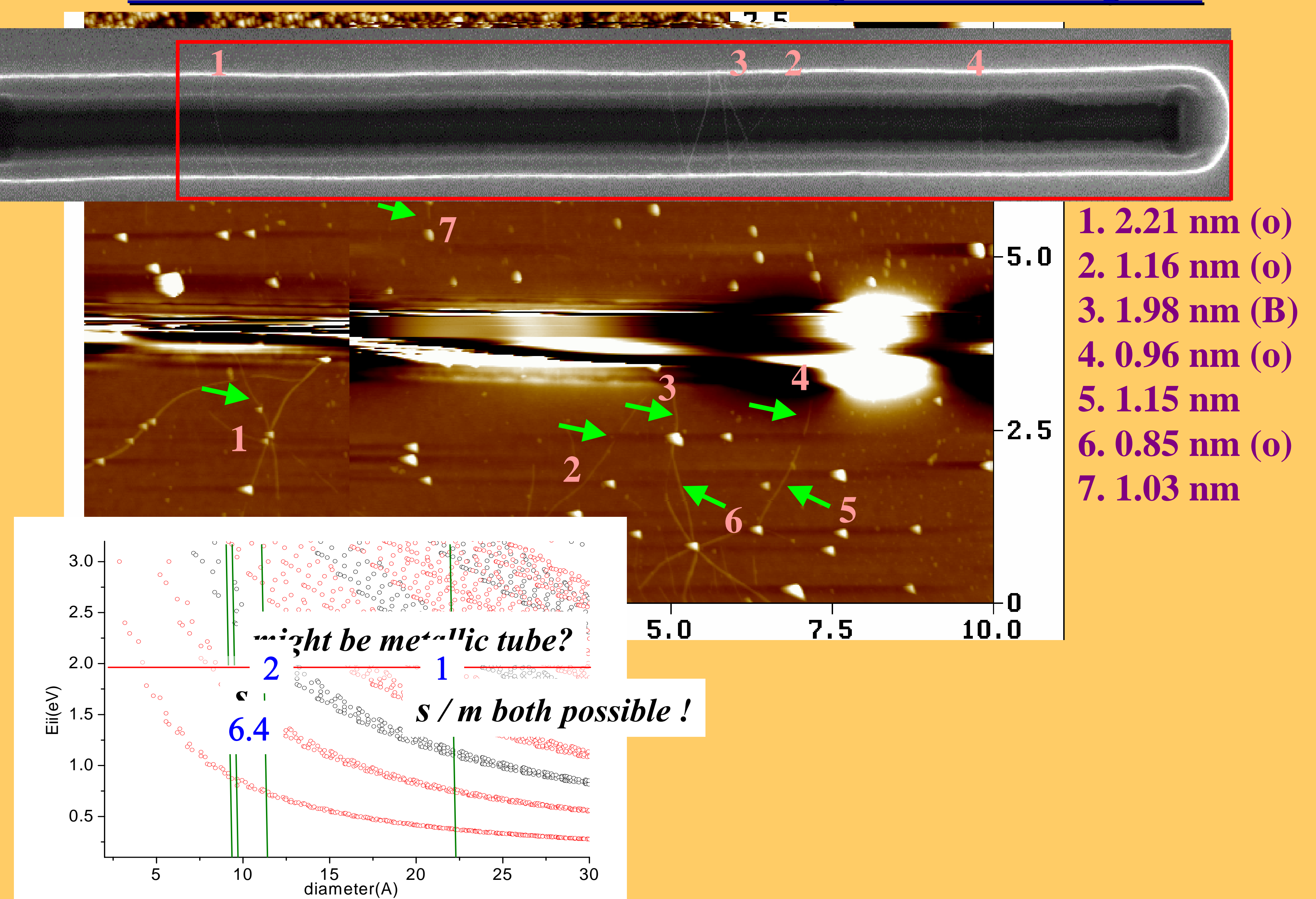
RBM

Determine SWNT diameter by AFM analysis



Avg. diameter = 0.78 ± 0.01nm

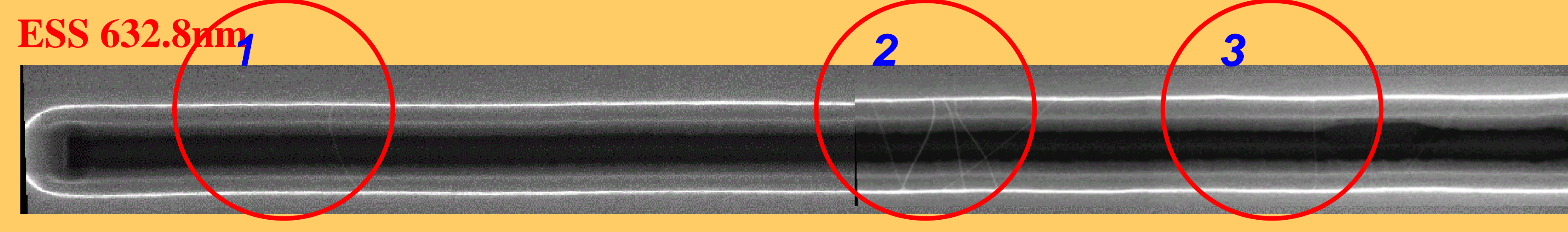
Determine SWNT diameter by AFM analysis



1. 2.21 nm (o)
2. 1.16 nm (o)
3. 1.98 nm (B)
4. 0.96 nm (o)
5. 1.15 nm
6. 0.85 nm (o)
7. 1.03 nm

compared the AFM result with μ-Raman measurement

ESS 632.8nm



1. (1:dt=2.209nm) ω_{G-} : 1570.7 cm^{-1} ω_{G+} : 1589.4 cm^{-1} :
   ℓ = 91.25 → might be metallic ! [o]
2. (6:dt=1.162nm) ω_{G-} : 1571.9 cm^{-1} ω_{G+} : 1591.3 cm^{-1} :
   ℓ = 26.19 → might be semiconducting ! [o]

   (2:dt=0.854nm) ω_{G-} : 1571.9 cm^{-1} ω_{G+} : 1591.3 cm^{-1} :
   ℓ = 14.15 → might be semiconducting ! [x]

$$\omega_{G^-} = \omega_{G^+} - \frac{\ell}{d_t^2}$$

3. (4:dt=0.957nm) ω_{G-} : 1576.3 cm^{-1} ω_{G+} : 1591.8 cm^{-1} :
   ℓ = 14.20 → might be semiconducting ! [o]

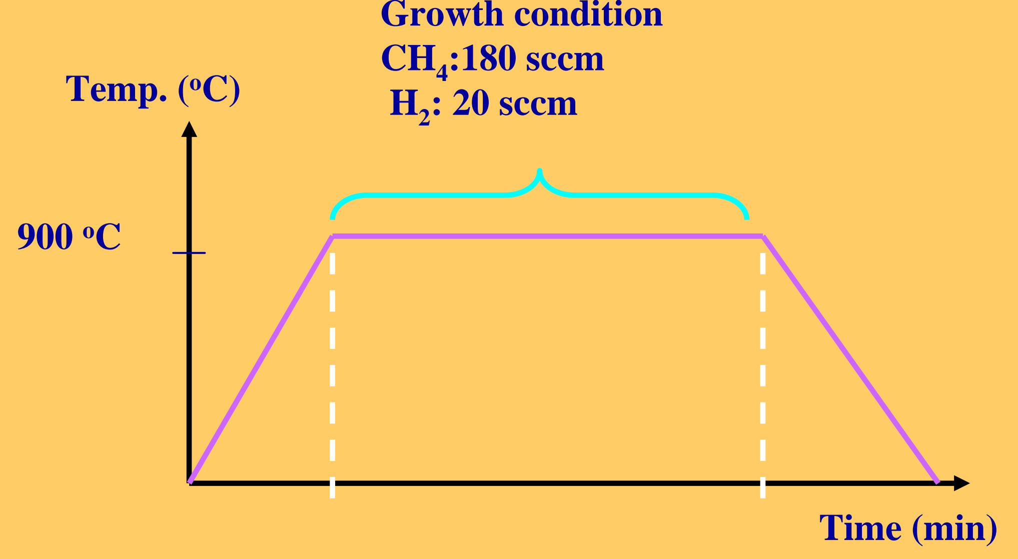
in the same growth process and even in the same trench

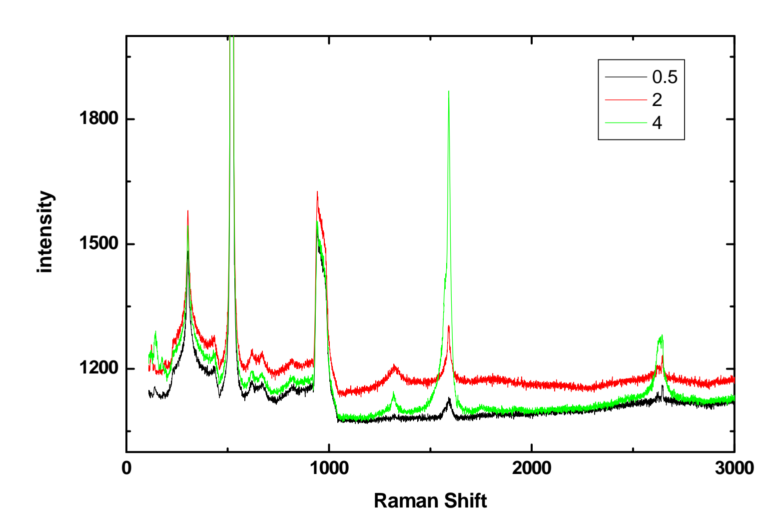
→ *existing of mixing semiconducting & metallic tubes!*

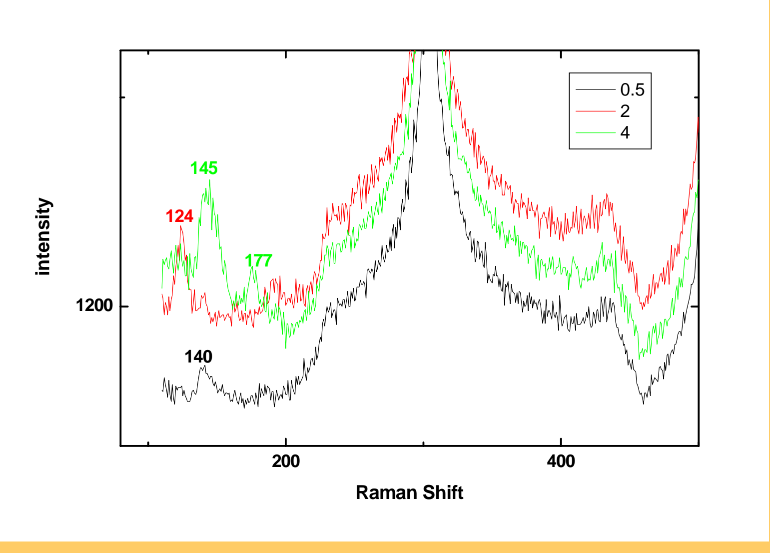
Diameter Distribution Control

Different deposition rates

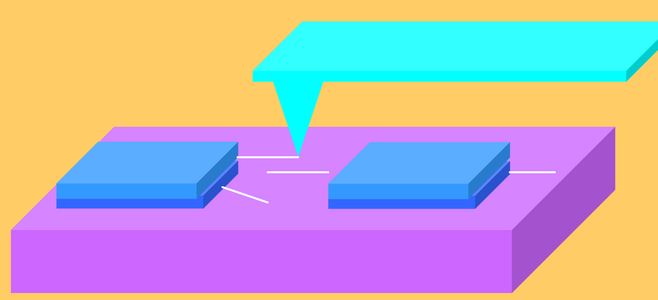
Deposition rate of SiO_2 layer	0.5 Å/s	2 Å/s	4 Å/s
Thickness of nickel layer	3.3 nm	4 nm	3.5 nm



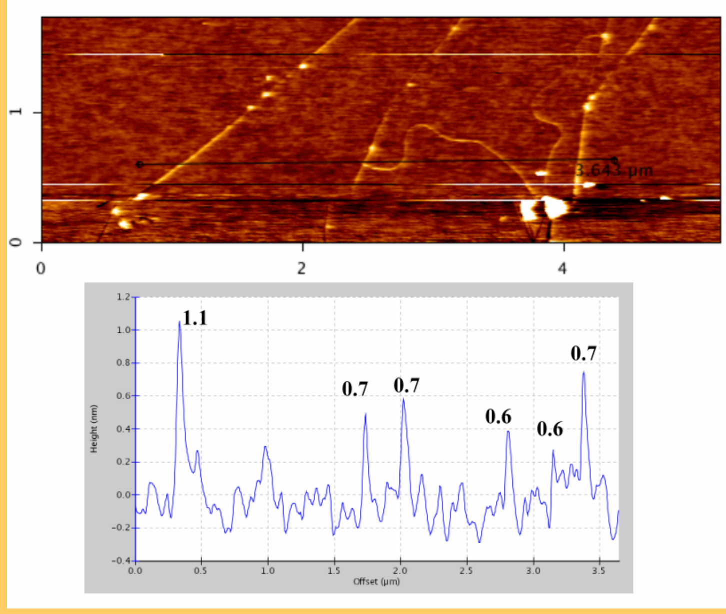




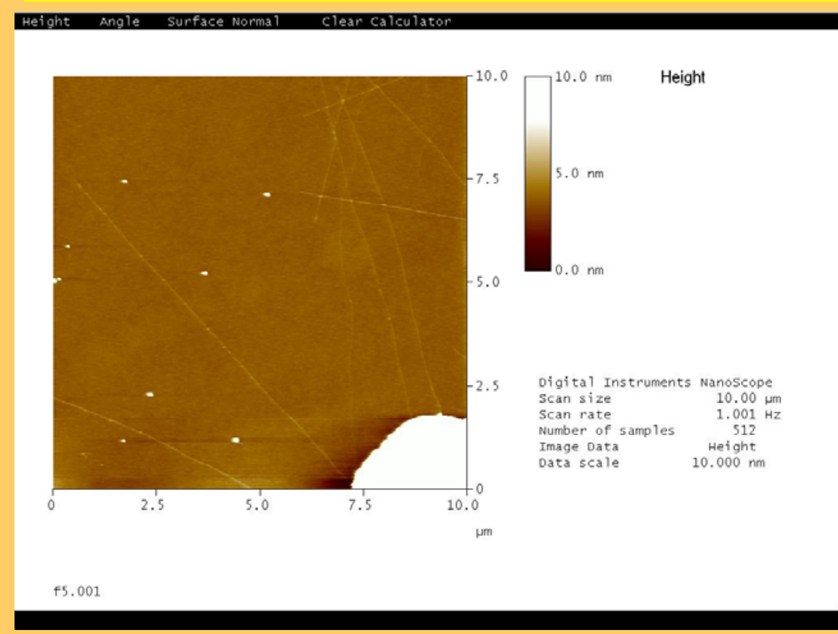
SWNTs Characterizations

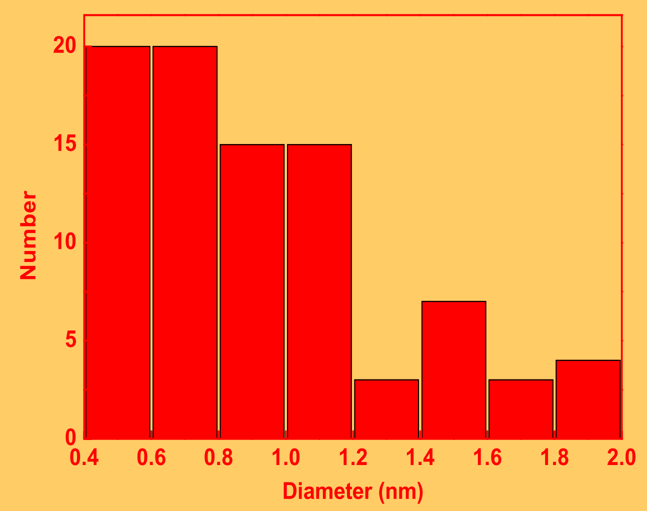


ESS NE101 (JPK AFM)

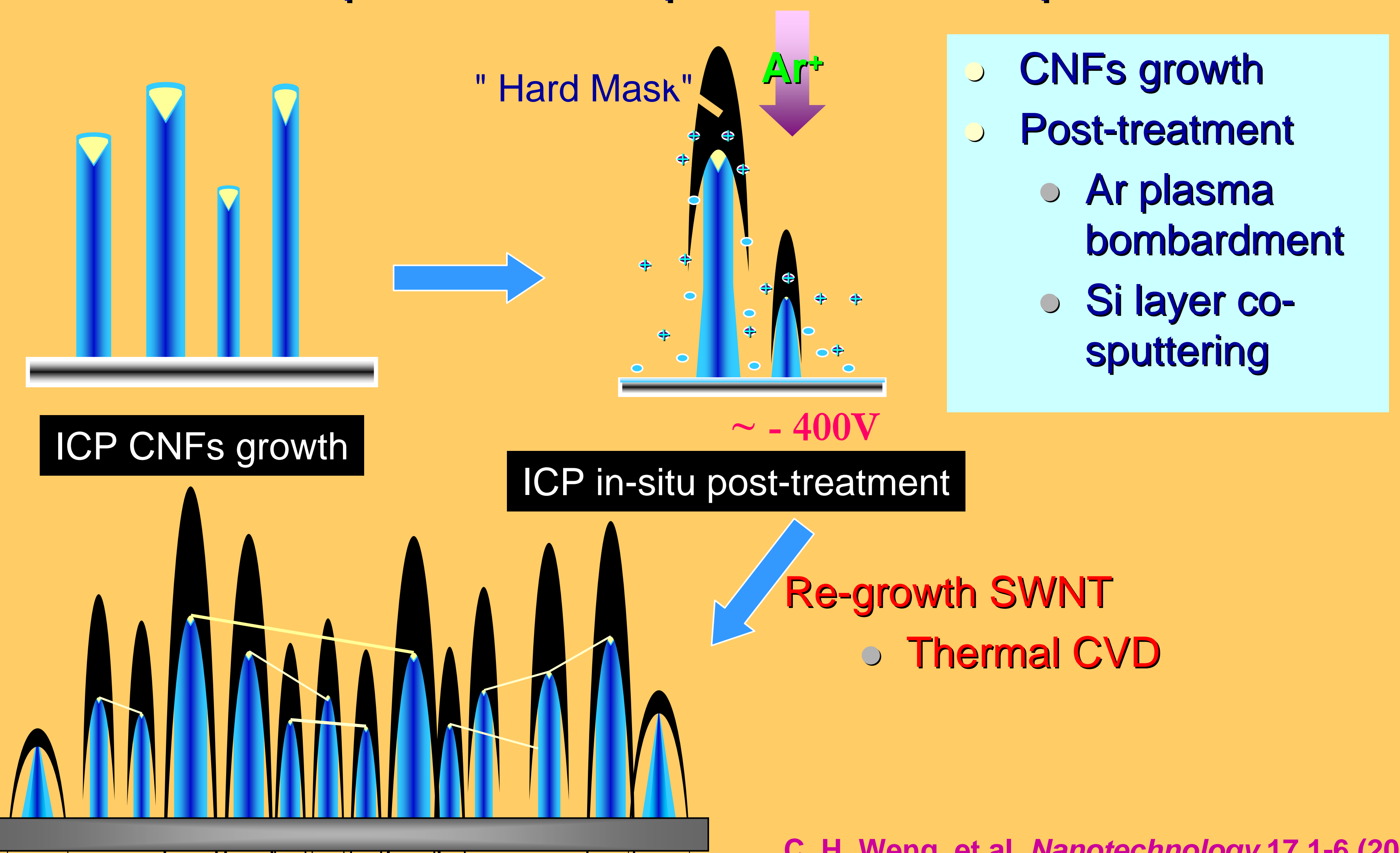


SiO_2 substrate +Ni + SiO_2 (0.5 Å/s)





Direct synthesis of SWNTs crossing plasma sharpened CNFs tips



C. H. Weng, et al, *Nanotechnology* 17 1-6 (2006)

Controlled *in-situ* Growth of Single-walled Carbon Nanotubes for Field-Effect-Transistor Application

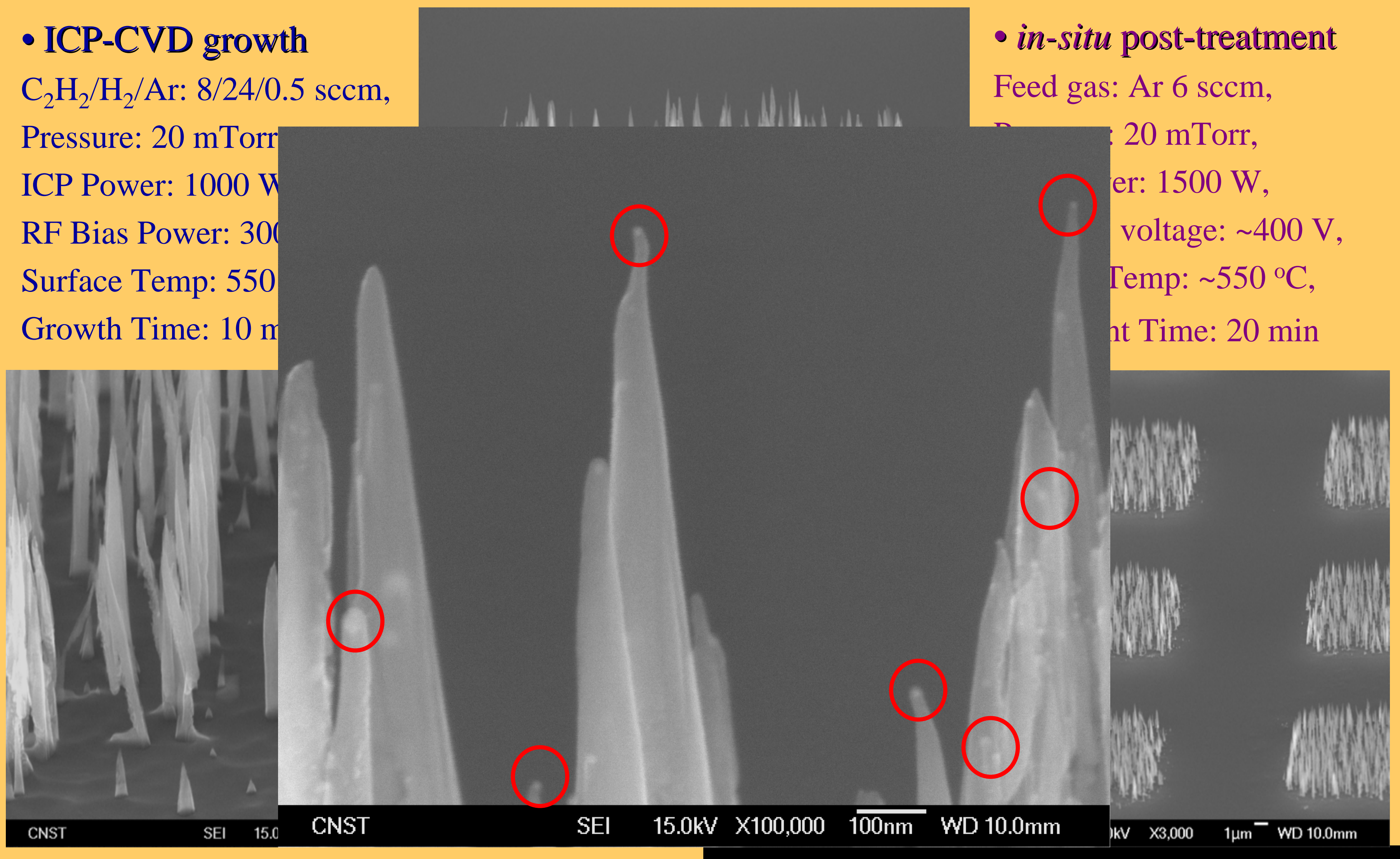
Direct synthesis of suspended SWNTs using sharpened CNFs as templates

- **ICP-CVD growth**

$C_2H_2/H_2/Ar$: 8/24/0.5 sccm,
Pressure: 20 mTorr
ICP Power: 1000 W
RF Bias Power: 30
Surface Temp: 550
Growth Time: 10 m

- ***in-situ* post-treatment**

Feed gas: Ar 6 sccm,
: 20 mTorr,
er: 1500 W,
voltage: ~400 V,
Temp: ~550 °C,
nt Time: 20 min

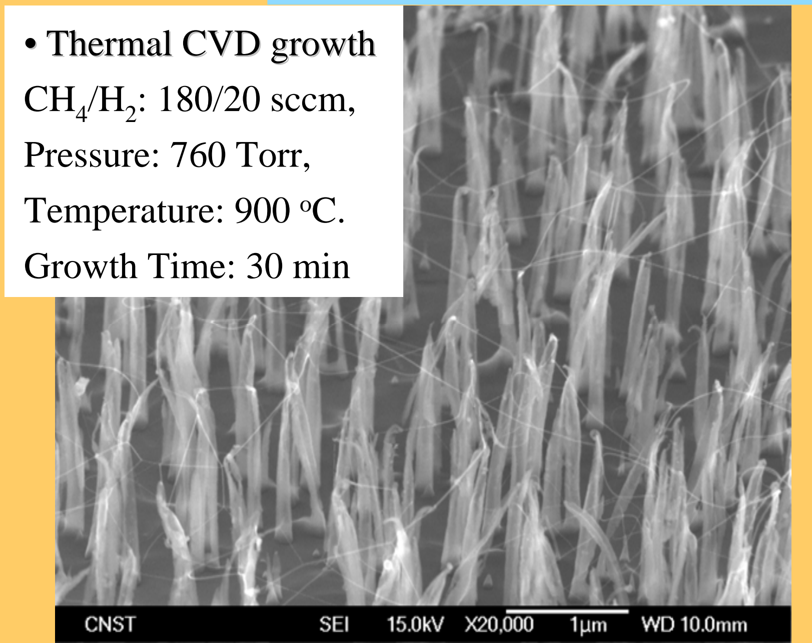


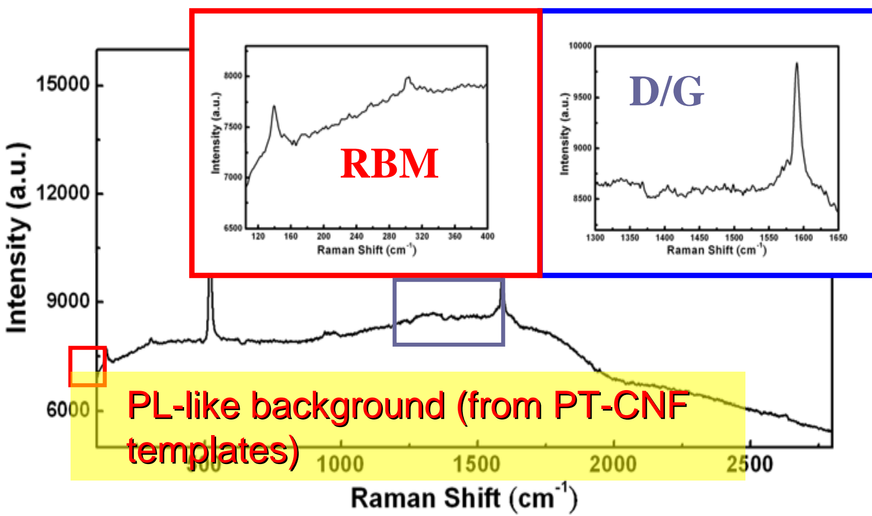
C. H. Weng et al, *Appl. Phys. Lett.* 85, 4732 (2004).

Controlled *in-situ* Growth of Single-walled Carbon Nanotubes for Field-Effect-Transistor Application

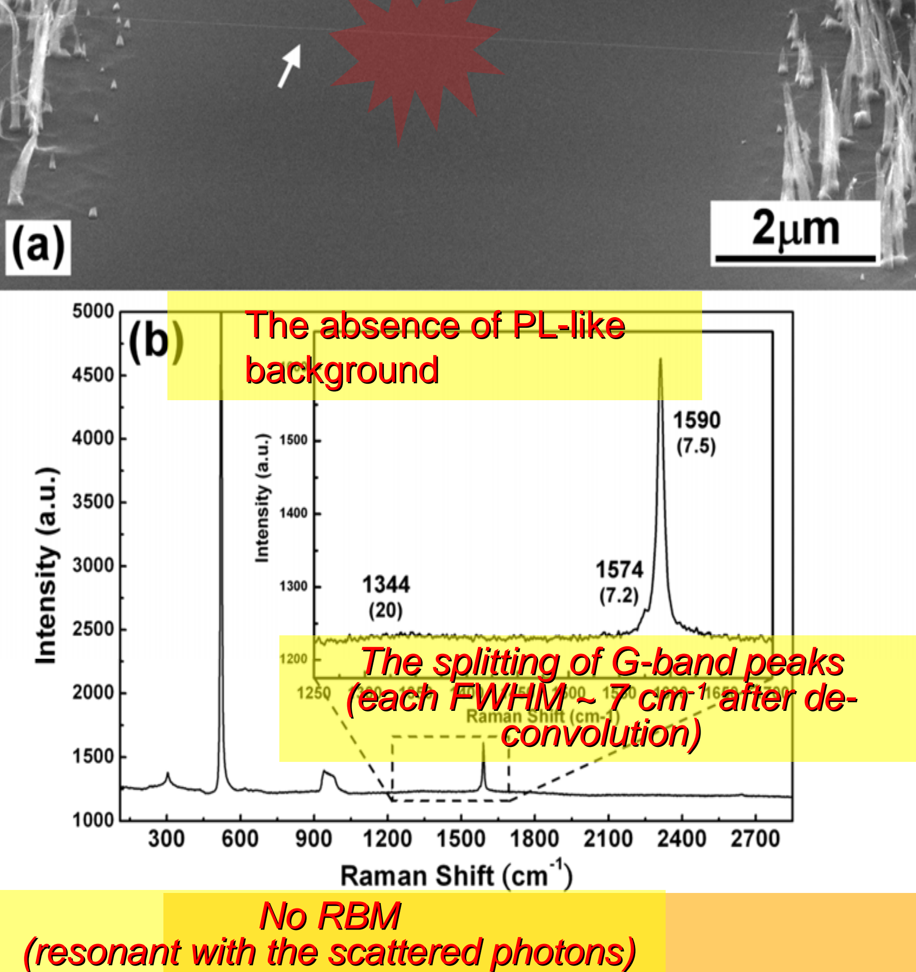
- Thermal CVD growth

CH_4/H_2: 180/20 sccm,
Pressure: 760 Torr,
Temperature: 900 °C.
Growth Time: 30 min





Raman spectrum at *one SWNT level*



C. H. Weng et al, *Nanotech.* 17 (2006) 1-6.

“The principles of physics do not speak against the possibility of manufacturing things atom by atom……”

“At the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects.
The problems of manufacturing and reproduction of materials will be quite different.”

F=ma

Richard Feynman
“There’s Plenty of Room at the Bottom”
1959, Caltech

Acknowledgement～

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Funded by:

National Science Council

Materials Research Laboratories, ITRI

Nano-Architect Research Corpoation

Center for Nano Science & Technology, University System of Taiwan

Center for Measurement Standard, ITRI (for micro electron gun)